ANALYTICA CHIMICA ACTA

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. PAUL-E. WENGER, 8 Rue St. Victor, Geneva (Switzerland) or to

Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. (U.S.A.)

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Legends for figures should be typed on a **separate** page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in **thin pencil**. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

Standard symbols should be used in line drawings. The following are available to the printers:

▼ ▽ ■ □ ● ◎ ▨ ▣ ⊕ ▤ ▪ ▣ + ×
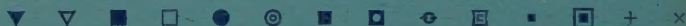
All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places. The abbreviations of journals should conform to those adopted by *Chemical Abstracts* (see Vol. 50 (1956) 1 J – 314 J). A summary of 50 to 200 words should be included. Authors of papers in French or German are encouraged to supply also a translation of the summary in English.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta will have six issues to the volume, approx. 600 pages per volume, two volumes per year.

Subscription prices (post free): $ 15.— or £ 5.7.6. or Dfl. 57.— per volume; $ 30.— or £ 10.15.- or Dfl. 114.— per year.
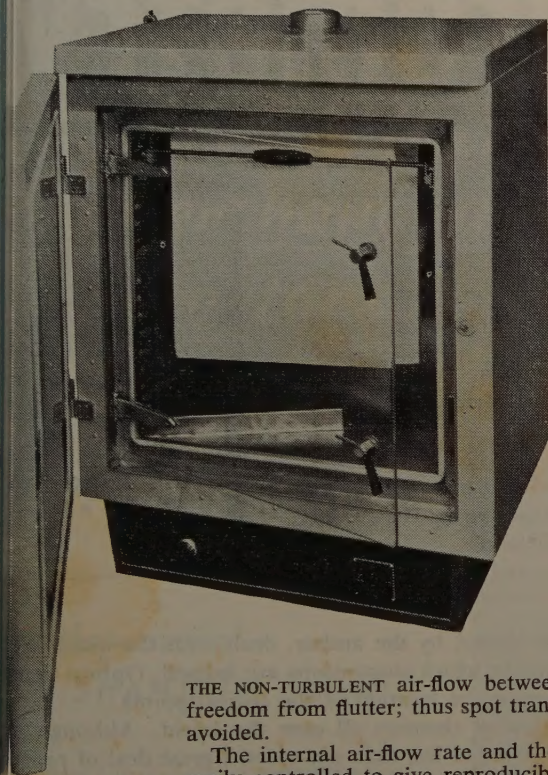
For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, Spuistraat 110 – 112, Amsterdam-C., The Netherlands

Heterometry

M. Bobtelsky

Table of contents:

Heterometry, a method of analysis devoloped by the author, deals with the quantitativ photometric study of chemical reactions in which suspensions are formed. Optical densit curves are measured in order to determine the location of the critical points.

This method has attracted the attention of chemists all over the world. Although th development of heterometry covers a period of less than ten years, a great deal of progres has been made and the author has attempted to summarize what has been achieved i this relatively short time.

Much of the book has been devoted to the use of heterometry in the rapid analytica determination of traces of metals, other ions or compounds, in the presence of a larg excess of other substances, without any previous separation. The book contains a wealt of original material, generously supplemented with tables and figures, which demonstrat how hitherto unsolved problems can easily be solved by heterometry. Very often a fet tenths of a milligram of material is sufficient for a whole investigation. The instrumenta tion as well as the various aspects of heterometry are thoroughly reviewed so that on th basis of information given chemists will be able to tackle their own problems by hetero metry. This method will be of especially great value to all research workers as well as t industrial chemists working in the fields of analytical and microanalytical chemistry complex chemistry, study of composition and structure of intermediates, lakes, com plicated organic nitrogen compounds etc.

Just published:

CHROMATOGRAPHIC REVIEWS

Volume 2
Covering the year 1959

Progress in Chromatography, Electrophoresis and related methods

Edited by MICHAEL LEDERER

The success of Volume 1 of this series, as well as the numerous requests for reprints of review articles in the Journal of Chromatography, have justified the continuation of the publication of the reviews in book form. All reviews have first been published in the Journal of Chromatography, those which were not originally in English were subsequently translated.

$6\frac{1}{2}'' \times 9\frac{1}{2}''$ *viii + 195 pages*   *29 tables*   *49 illus.*   *1960*

CONTENTS:

TITRATION OF MERCURY(II) WITH SODIUM TETRAPHENYLBORON*

A. HEYROVSKÝ

Laboratory of the 2nd Medical Clinic, Charles University, Prague (Czechoslovakia)

(Received September 23rd, 1959)

uring an investigation concerning the possibilities of a mercurimetric titration of e insoluble tetraphenylboron precipitates of potassium and of some organic bases, e reaction of sodium tetraphenylboron with mercuric and mercurous ions was udied. There is in the literature some controversy on the nature of the precipitates sulting from the reaction. The end-product of the reaction of an excess of mercuric as with tetraphenylboron is known to be a phenylmercuric salt[1], but some workers nsider that during the reaction mercuric or mercurous tetraphenylboron is formed[2,3]. e have found that the titration of tetraphenylboron with mercuric salts (nitrate, rchlorate) proceeds in two steps. In the first step of the titration, which can be llowed up by potentiometry, polarometry or polarography[4], 3 equivs. of mer-ry(II) are consumed per mole of tetraphenylboron with the formation of diphenyl-ercury and phenylboric acid[5]. The mercuric tetraphenylboron reported in the erature[2] is in fact diphenylmercury and consequently the mercurous tetraphenyl-oron of the literature[2] is a mixture of diphenylmercury and metallic mercury. ercury tetraphenylboron, if any is formed during the titration, must be extremely uickly decomposed to diphenylmercury and phenylboric acid. In the second step the titration the added mercuric ions react with diphenylmercury and with nenylboric acid, and the corresponding phenylmercuric salt is found after a con-umption of a total of 8 equivs. of mercury(II) per mole of tetraphenylboron[4,5]. The soluble diphenylmercury which separates in the first step dissolves again during the cond step and the solution at the end-point is clear, when the titration is performed ith mercuric nitrate or perchlorate, since phenylmercuric nitrate and perchlorate e sufficiently soluble in water.

In the reverse titration, when mercury(II) is titrated with a solution of sodium traphenylboron, two steps are again noted[4-6]. In the first, 0.25 mole of sodium tetra-henylboron are consumed per mole of mercury(II), phenylmercuric salt is formed nd the liquid remains clear. In the second step, phenylmercuric salt reacts with the trant and the solution becomes turbid. Insoluble diphenylmercury separates, until bout 0.5 mole of tetraphenylboron are consumed according to:

$$4\ Hg(NO_3)_2 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgNO_3 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$
$$\text{(first step)}$$
$$4\ C_6H_5HgNO_3 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgC_6H_5 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$
$$\text{(second step)}$$
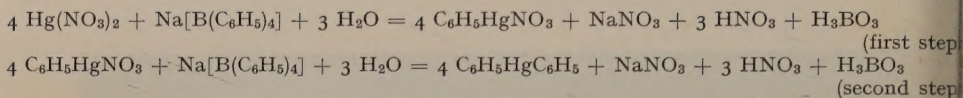
At present the literature on sodium tetraphenylboron is concerned primarily with the determination of potassium, ammonium and organic bases. It seemed interesting to extend the use of the reagent to the direct titration of mercury. A gravimetric determination of mercury in the form of diphenylmercury after precipitation with sodium tetraphenylboron has already been described from this laboratory[5].

EXPERIMENTAL

Reagents

0.020 M sodium tetraphenylboron was prepared by dissolving about 2 g of reagent grade sodium tetraphenylboron "Kalignost" in twice distilled water, clearing with alumina if turbid and making up to 250 ml with twice distilled water. The titre of the solution was determined by titrating a standard solution of mercuric nitrate as described in the procedure. An appropriate volume of water was then added to obtain a 0.020 M solution. Alternatively the titre was checked by potentiometric titration with silver nitrate[7]. The solution was stable for a week or more, provided that its pH was about 8.5. The titre should be checked daily.

0.16 N mercuric nitrate, containing 16.0488 mg of Hg/ml, was prepared by dissolving the exactly weighed amount of thrice distilled metallic mercury in concentrated nitric acid, boiling to expel nitrogen oxides and diluting to volume with twice distilled water.

Procedure

An aliquot of the sample was diluted to contain about 5–50 mg of mercury(II) and not more than 1 mg/ml, and titrated under constant stirring with the solution of sodium tetraphenylboron from a microburet. After the addition of each drop of titrant, a turbidity of diphenylmercury developed but rapidly dissolved on swirling. When all the mercury had been converted to phenylmercuric nitrate, the excess of titrant caused a persistent turbidity of diphenylmercury. The end-point was sufficiently sharp and could be recognized within 0.01 ml of the titrant.

1 mole of sodium tetraphenylboron corresponds to 4 moles of mercury(II), hence 1 ml of 0.020 M sodium tetraphenylboron corresponds to 16.0488 mg of mercury(II).

The titration could be performed in neutral or slightly acidic (up to 0.05 N HNO$_3$ or HClO$_4$) solutions or in solutions buffered with sodium acetate. The correct dilution of the sample was important. When it was not diluted sufficiently, amorphous or crystalline particles of phenylmercuric nitrate separated during the titration, making the exact recognition of the end-point difficult and causing low results. These particles however could readily be differentiated from the turbidity of diphenylmercury. Provided that the dilution of the sample was satisfactory, the volume of the titrated solution was not critical. In actual experiments about 15 ml were used for 5–10 mg of mercury(II), about 40 ml for 5–30 mg and about 60 ml for 5–50 mg. When greater amounts of mercury(II) were present, correspondingly larger volumes had to be used for the titration.

Interferences

In solutions buffered with sodium acetate the interferences of several ions could be eliminated by a suitable chelating agent. When ethylenediaminetetraacetic acid was added, mercury could be titrated in the acetate medium even when an excess of Cu, Zn, Mg, Ca, Mn, Ni, etc., was present.

in a slightly acidic solution no interference was observed from Zn, Cu, Ba, Ni, Ca, Co, Pb, Al, Bi, etc.

Common anions (NO_3^-, ClO_4^-, PO_4^{-3}, ClO_3^-, SO_4^{-2}, NO_2^-, $B_4O_7^{-2}$, AsO_4^{-3}) did not interfere. Any anion which gives insoluble phenylmercuric salts (Cl^-, Br^-, I^-, CNS^-) caused a turbidity at the beginning of the titration making the determination impossible.

Mercury(I) gave at the beginning of the titration a fine gray precipitate of metallic mercury and made the determination difficult.

Any ion which precipitates with sodium tetraphenylboron interfered when present in excess of the mercuric ions. However, in slightly acidic solution the titration gave good results even when the amount of potassium present was 2–3 times that of mercury(II). On the other hand, silver ions could be tolerated only when the amount was about half that of mercury(II). Obviously, the affinity of the tetraphenylboron complex for mercuric ions is markedly higher than that for the other ions. For example, when a solution of potassium and mercuric ions was titrated with sodium tetraphenylboron, the added reagent was first rapidly decomposed by mercuric ion, forming phenylmercuric salt, then phenylmercuric salt reacted to form diphenyl-mercury and in fact no tetraphenylboron was available to precipitate potassium. When all the mercury present has been bound as diphenylmercury, the titrant no longer reacted with it and insoluble potassium tetraphenylboron could separate. With relatively high concentrations of potassium, some insoluble tetraphenylboron was precipitated simultaneously with the formation of phenylmercuric salt; this reacted only slowly with the mercury(II) present. Silver tetraphenylboron is much more insoluble than the potassium compound, therefore silver interferes in markedly lower concentrations.

RESULTS

Numerous titrations of standard solutions of mercuric nitrate and mercuric per-chlorate were performed. Some figures are presented in the table. The error did not usually exceed 1%. When the content of mercury was determined by the present method in various materials, e.g. mercuric compounds, organic mercurials and

TABLE I

Hg taken mg	0.020 M sodium tetraphenylboron consumed ml	Hg found mg	Difference %
2.0	0.12	1.93	− 3.50
2.0	0.13	2.08	+ 4.00
5.0	0.31	4.98	− 0.40
5.0	0.31	4.98	− 0.40
10.0	0.63	10.10	+ 1.00
10.0	0.62	9.95	− 0.50
15.0	0.93	14.93	− 0.50
15.0	0.94	15.08	+ 0.50
20.0	1.24	19.90	− 0.50
20.0	1.25	20.05	+ 0.25
25.0	1.56	25.00	± 0.00
25.0	1.57	25.20	+ 0.75
30.0	1.87	30.00	± 0.00
30.0	1.87	30.00	± 0.00
30.0	1.86	29.90	− 0.30

pharmaceutical preparations after a suitable mineralisation, the results obtained agreed well with those obtained by the standard titrimetric procedure using thio cyanate.

SUMMARY

A direct visual titration of mercury (II) with sodium tetraphenylboron ("Kalignost") is described Phenylmercuric salts are formed and the end-point is indicated by a turbidity of insoluble diphen ylmercury.

RÉSUMÉ

Une méthode est décrite pour le titrage direct du mercure(II) au moyen de tétraphénylborate d sodium. La formation de diphénylmercure, insoluble, indique le point final.

ZUSAMMENFASSUNG

Es wird eine direkte Titration der Quecksilber(II)-Ionen mit Tetraphenylbornatrium (,,Kali gnost") beschrieben. Der Endpunkt ist erreicht, sobald sich die Lösung durch Ausscheidung vor Diphenylquecksilber zu trüben beginnt.

REFERENCES

1 G. Wittig and P. Raff, *Ann.*, 573 (1950) 195.
2 W. W. Wendlandt, *Chemist Analyst*, 46 (1957) 38.
3 R. Montequi, A. Doadrio and C. Serrano, *Anales real. soc. Españ. fís. y quím. Madrid*, Ser. B 53 (1957) 447.
4 A. Heyrovský, *Collection Czech Chem. Communs*, in the press.
5 A. Heyrovský, *Z. anal. Chem.*, in the press.
6 A. Heyrovský, *Analyst*, in the press.
7 A. Heyrovský, *Collection Czech Chem. Communs*, 24 (1959) 170.

DETERMINATION OF PROTACTINIUM-233 IN IRRADIATED THORIUM

J. J. McCORMACK, F. H. CRIPPS and W. A. WIBLIN

Atomic Weapons Research Establishment, Aldermaston, Berkshire (Great Britain)

The increasing interest in the $^{233}U/^{232}Th$ fuel cycle for future reactors stresses the importance of being able to determine ^{233}U in thorium, since the rate of production of ^{233}U is a vital step in the analysis of performance of experimental assemblies Neutron capture in ^{232}Th produces the sequence:

$$^{232}Th\ (n,\ \gamma)\ ^{233}Th \xrightarrow[23.3\ min]{\beta} {}^{233}Pa \xrightarrow[27.4\ days]{\beta} {}^{233}U\ (1.62 \cdot 10^5\ years)$$
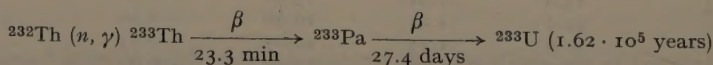
^{233}Th is rather short-lived and cannot be separated chemically from ^{232}Th, while ^{233}U has a low specific activity on account of its long half-life. The intermediate daughter ^{233}Pa is therefore chosen for the assessment during the initial stages of a reactor

experimental assembly, before any appreciable amount of ^{233}U has grown in.
The method was designed to separate amounts ranging from 200–10^5 d.p.m. of
Pa in 1-g portions of irradiated thorium metal containing 10^4 to 10^9 fissions. The
ld of the chemical process was determined from the recovery of ^{231}Pa tracer added
known amount. On account of the low activity of some of the samples to be analysed,
was desirable to use a fairly simple chemical separation scheme giving a high yield.
od decontamination was essential, since in the presence of the 27.4 day ^{233}Pa, any
mitting long-lived impurity would not be detected easily without prolonged count-
of the final sources.

Owing to the ease with which protactinium hydrolyses and forms adsorbable col-
ds in aqueous solution, it is necessary to carry out chemical processes in strong acid
complexing solutions using polythene apparatus. Solvent extraction and ion ex-
ange are attractive methods under these conditions. A number of organic solvents
e available for the extraction of protactinium from strong acid solution and are
scussed by KATZ AND SEABORG[1] and HYDE[2].

Di-isopropyl carbinol was considered to be the most suitable solvent for the scheme
account of its efficiency for protactinium and high selectivity in strongly acid
stems. Protactinium is strongly adsorbed on anion-exchange resin (e.g. Amberlite
G. 400) from 6 N hydrochloric acid and is easily eluted by the same acid containing
5 N hydrofluoric acid[3].

For the measurement of the ^{233}Pa radiation, β-counting was preferred rather than
counting since the latter required a higher source activity and more elaborate equip-
ent for accurate determination.

The β-rays of ^{233}Pa are of low energy and are accompanied by large numbers of
nversion electrons. The efficiency of end-window counters for this type of emission
nnot be calculated accurately from geometrical consideration and calibration by
me other counting method must be used. The method reported here is similar to
at described by CRIPPS AND WEALE[4] for the absolute counting of ^{239}Np and that of
cISAAC AND FREILING[5] for ^{233}Pa, involving a source of ^{233}Pa in equilibrium with
s parent ^{237}Np whose disintegration rate was determined accurately by α-counting.
alibration of an end-window gas flow proportional counter using this source gave
od agreement with the efficiency obtained using a pure ^{233}Pa source which had
en standardised by 4 π-counting. Since the final sample sources contained added
Pa, these and the standard ^{237}Np source were β-counted using a 5 mg/cm^2 absor-
er to cut out the alpha particles.

EXPERIMENTAL

hemical

For the development of the scheme, synthetic solutions of 1 g of thorium in 3 ml
f 6 M nitric acid containing a known amount of ^{231}Pa tracer (about 200 d.p.m.) and
ome 24 h old fission products equivalent to 5 × 10^{12} fissions were prepared. The
olvent extraction stage showed a 90% yield for the ^{231}Pa but produced sources
ontaminated with about 2 × 10^4 d.p.m. of β–γ radiation most of which appeared
o be ^{99}Mo, ^{97}Zr and ^{95}Zr. These impurities were removed by passing the solution in
N hydrochloric acid through an anion-exchange column which retained only the
rotactinium and molybdenum and by eluting the protactinium with 6 N hydrochloric
cid containing 0.5 N hydrofluoric acid which removed the protactinium as the fluo-

ride complex leaving the molybdenum on the column[3]. After this stage resultant sources contained about 1.5×10^3 d.p.m. of impurities and the decay curves showed two components having half lives of 70 min and about 20 h respectively, the former being predominant. Since over 24 h had elapsed from the last time of irradiation the short-lived component must have separated from a longer lived parent during the chemical purification. Examination of possible fission product species and their yields showed that the short-lived component must be due to ⁹⁷Nb, the daughter of 17 h ⁹⁷Zr, the latter species accounting for the longer-lived component.

After a few days these activities decayed leaving a residual long-lived β-emitter of about 90 d.p.m. The decontamination achieved was considered satisfactory for samples containing the larger amounts of ²³³Pa and fission products. By increasing the concentration of the hydrochloric acid in the eluting mixture to 11 N all niobium should be held on the column since the distribution coefficient for the adsorption of Nb^{+5} is about 60 at this concentration as against 6 for 6 N hydrochloric acid–0.5 hydrofluoric acid mixture[3].

Repeated experiments with varying amounts of fission products added gave sources which showed a constant activity of about 30 d.p.m. due to the γ-radiation of the ²³¹Pa tracer. Examination of the complex decay scheme of this isotope made it clear that conversion electrons and the X-rays produced by the L-shell conversion of the gamma rays in the 27–46 keV region would give counts in the β-counter equivalent to about 10% of the alpha disintegration rate. Since these counts were proportional to the alpha radiation of the tracer, the ratio was determined experimentally and allowed for in the final sources.

Counting of the sources

By 4 π-counting

²³³Pa was obtained by irradiation in B.E.P.O. Harwell of thorium nitrate (AnalaR) and purified by the above chemical method. Sources were prepared by weighing out portions of the ²³³Pa solution onto thin plastic foils (VYNS)[4] and also onto stainless steel discs.

The VYNS sources were counted in a $4 \pi \beta$-counter (A.E.R.E. Type 1364) assuming an efficiency of 100%. This assumption is based on the results of PATE AND YAFFE who showed that the efficiency for this type of counter with β-emission of similar energy is about 99%. As the β-emission is accompanied by coincident conversion electrons which are counted with high efficiency, the overall efficiency of the 4π counter must be greater than this. Comparison of the steel disc sources with the 4π sources gave an efficiency of 0.287 ± 0.01 for the 2-in. diameter end-window counter with the source at a distance of 1 cm.

By ²³⁷Np

Stainless steel disc sources were prepared from a solution of ²³⁷Np containing ²³³Pa in equilibrium and standardized by comparison with a stronger alpha source mounted similarly, and of known disintegration rate, in an α-scintillation counter (A.E.R.E. Type 1093). From the β-count rate of these steel disc sources, the end-window counter efficiency was found to be 0.296 ± 0.008. These results compare favourably with later work by BROWN AND LARGE[8] whose similar experiments gave

efficiency of 0.307 $\pm$ 0.004 for the 4 π calibration and an efficiency of 0.299 $\pm$ 0.006 using a ^{237}Np – ^{233}Pa source. The 4 π results have a larger scatter than those of the ^{237}Np – ^{233}Pa, due to the greater sensitivity of the 4 π counter to differences in source thickness, but the results agree within experimental error. During their experiments, BROWN AND LARGE purified some of the ^{237}Np and allowed the ^{233}Pa to grow into equilibrium, in order to check the purity of the source, and their results confirmed the validity of the method.

In the final sources the chemical yields of the analyses were found by α-scintillation counting of the recovered ^{231}Pa.

EXPERIMENTAL

Apparatus

Polythene ion-exchange columns containing Amberlite C.G. 400 resin, volume 50 mm $\times$ 4 mm, previously conditioned with 6 N hydrochloric acid. Small polythene beakers of 10-ml capacity. All solvent extractions and washings carried out in 5-ml polythene ampoules drawn out to a point[6]. Lustroid tubes of 3-ml capacity for transfer of liquid phases. Stainless steel discs of 1 in. diameter. End-window proportional β-counter. Alpha scintillation counter. A standardized source of ^{237}Np in equilibrium with its ^{233}Pa daughter.

Reagents

Concentrated nitric acid containing the equivalent of 0.01 N hydrofluoric acid, 6 N hydrochloric acid containing the equivalent of 0.5 N hydrofluoric acid, 11 N hydrochloric acid containing the equivalent of 0.5 N hydrofluoric acid.
Di-isopropyl carbinol saturated with 6 M nitric acid. Pure ^{231}Pa tracer solution standardized.

Procedure

Add about 1 g of the irradiated thorium metal and a known amount of ^{231}Pa tracer (about 60 d.p.m.) to concentrated nitric acid containing the equivalent of 0.01 N hydrofluoric acid in a platinum dish. Dissolve the metal by heating, adding more acid when necessary. Evaporate the final solution to about 1 ml and dilute with water to 3 ml. Extract the protactinium by twice shaking for two minutes with 1 ml of di-isopropyl carbinol equilibrated with 6 M nitric acid, and wash the combined organic phase three times with 1 ml 6 N hydrochloric acid. Back extract the protactinium by shaking twice for two minutes with 1 ml of 6 N hydrochloric acid–0.5 N hydrofluoric acid mixture, wash the combined aqueous phase with 1 ml of the organic reagent, and discard the latter. Evaporate the aqueous solution to dryness in a small polythene beaker on a water bath and using a jet of air. Dissolve the residue in 1 ml of 6 N hydrochloric acid and put through the ion-exchange column, followed by a further 6 ml of 6 N hydrochloric acid and reject the effluent. Elute the protactinium using 3 ml of 11 N hydrochloric acid–0.5 N hydrofluoric acid mixture and evaporate the effluent to dryness in a polythene beaker. Dissolve the residue in a small amount of 6 M nitric acid, and evaporate on a 1-inch stainless steel disc.
Determine the disintegration rate of the source by counting the ^{233}Pa β-emission in an end-window β-counter with a 5 mg/cm^2 absorber, and comparing with a similarly mounted standard source of ^{237}Np of known activity in equilibrium with its ^{233}Pa daughter.
Count the source in an α-counter and determine the disintegration rate of the recovered ^{231}Pa. When this compared with the original amount put in will give the factor required to convert the ^{233}Pa disintegration rate into the absolute amount present in the original sample.
Note: A source of the ^{231}Pa should be prepared, and β-counted in order to determine the contribution of the γ-emission. This is proportional to its α-disintegration rate and the amount may therefore be calculated for the appropriate quantity of tracer in each sample and deducted from the total β-count.

RESULTS AND CONCLUSIONS

The initial experiments showed that there was adequate decontamination to allow the ^{233}Pa to be directly counted. However in order to allow for any losses during the chemical separation it was essential that complete isotopic exchange between the ^{231}Pa and the ^{233}Pa was obtained during the initial dissolution. Although this was

fairly certain since protactinium usually exists as Pa^{+5} in strongly acid solution, som
test runs were made in order to confirm the exchange.

Known amounts of ^{233}Pa obtained by the irradiation of thorium were added t
1-g samples of thorium metal, together with ^{231}Pa during dissolution. If isotopi
exchange occurred, then the known initial ratio of $^{233}Pa/^{231}Pa$ should also be foun
in the final sources.

TABLE I

Sample No.	Added initially d.p.m.		Recovered d.p.m.		$\dfrac{b}{a} = x$	$\dfrac{b_1}{a_1} = y$	$\dfrac{y}{x}$
	$^{231}Pa\,(a)$	$^{233}Pa\,(b)$	$^{231}Pa\,(a_1)$	$^{233}Pa\,(b_1)$			
1	426	56000	257	33000	131.500	128.400	0.977
2	360	15500	292	12400	43.050	42.460	0.986
3	389	3080	210	1680	7.918	8.000	1.010
4	300	1140	204	749	3.800	3.672	0.966
5	373	572	333	496	1.531	1.490	0.974
6	357	140	170	68.5	0.392	0.403	1.027
						mean	0.990 ± 0.024

In Table I the last column shows the initial and final ratios compared. The averag
value is 0.990 with a standard deviation of 2%, and allowing for the usual countin
errors, this shows that isotopic exchange was obtained.

The chemical method given above is simple and rapid, and gives a decontaminatio
of 10^6 at 24 h after irradiation, with a known yield of 70–80% determined by th
addition of ^{231}Pa tracer. Sources on stainless steel discs are easily prepared and ma
be counted in an end-window counter provided there is sufficient thickness of absorbe
to prevent ^{231}Pa α-particles from entering the counter. Allowances must be made fo
the contribution of ^{231}Pa gamma activity to the β-count rate. The absolute disinte
gration rate may be obtained by comparison with a standardized source of ^{237}Np-
^{233}Pa which constitutes a permanent standard for the calibration of end-windov
counters.

ACKNOWLEDGEMENTS

SUMMARY

A method has been devised for the absolute determination of ^{233}Pa in irradiated thorium meta
by counting the β-emission of chemically separated and purified sources. The counter was cali
brated by a source of ^{237}Np of known activity in equilibrium with its ^{233}Pa daughter, and checke
by 4π counting.

RÉSUMÉ

Les auteurs ont établi une méthode de dosage de ^{233}Pa dans le thorium irradié par comptag
des rayons β. Le compteur est calibré par une source de ^{237}Np, d'activité connue, en équilibr
avec ^{233}Pa.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von ^{233}Pa in bestrahltem Thorium durc
Zählung der β-Emission. Die Eichung des Counters erfolgte mit einer Quelle von ^{237}Np bekannte
Aktivität im Gleichgewicht mit ^{233}Pa.

REFERENCES

. J. KATZ AND G. T. SEABORG, *The Chemistry of the Actinide Elements*, Methuen and Co. Ltd., London 1957, Chapter 4, p. 71.
. K. HYDE, *Radiochemical Separation Methods for the Actinide Elements*, A/Conf. 8/P/728. 2 July 1955., p. 11.
. A. KRAUS AND F. NELSON, *A.S.T.M. Symposium on Ion Exchange and Chromatography in Analytical Chemistry*. Atlantic City, New Jersey 1956, Paper 23.
. H. CRIPPS AND J. W. WEALE. *J. Inorg. & Nuclear Chem.*, 7 (1958) 339.
. D. McISAAC AND E. C. FREILING, *Nucleonics*, 14, No. 10 (1956) 65–67.
. HERRINGTON AND D. G. VALLIS, *Chem. & Ind.*, London (1957) 808.
. D. PATE AND L. YAFFE, *Can. J. Chem.*, 33 (1955) 929.
. BROWN AND R. LARGE, *private communication*.

PECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM IN AIR AND DUST

R. H. A. CRAWLEY

English Electric Co. Ltd., Atomic Power Division, Whetstone (Great Britain)

INTRODUCTION

is well known that the handling of beryllium and its compounds can give rise very serious health hazards, if most stringent precautions are not taken. In any boratory or workshop where beryllium is handled, it is very important that all perations should be monitored to ensure that the operators are not subjected to ore than a permitted dosage of beryllium.

The whole problem is discussed by BROOKS[1].

The most serious hazard in the handling of beryllium is due to deposition of eryllium compounds in the lungs, causing either acute or chronic berylliosis. Surface ontamination can also be hazardous, because it is a potential source of aerial containation, and also because beryllium compounds on the skin can set up a very npleasant dermatitis, especially if they come into contact with cuts or abrasions. onitoring therefore takes two forms: samples of air are taken to ensure that the vel of aerial contamination is very low (see later), and samples of dust are taken om surfaces at appropriate positions.

The collection of samples from surfaces is a fairly simple procedure. A known rea of the surface, usually 1 m^2, is wiped carefully with a filter paper (a 5.5 cm Whatman No. 541 paper is suitable), when any loosely adhering deposit is transferred o the paper. This is then placed in a suitable container (*e.g.* a polythene envelope) nd taken to the analytical laboratory. The maximum acceptable level for surface ontamination is a matter for debate, and various factors must be taken into conideration in setting a limit for any particular type of surface.

Definite maximum permissible levels for beryllium in air have been recommende
by the United States Atomic Energy Commission[2] and have been widely accepte
in this country. These are that:

a. The concentration of beryllium in air should not exceed an average of 2 $\mu g/m$
over an 8-h working day in areas where beryllium is being handled.

b. The concentration of beryllium in air should not exceed 25 $\mu g/m^3$ for an
period however short.

c. The average concentration per month of beryllium in air, in the neighbourhoo
of an area where beryllium is handled, should not exceed 0.01 $\mu g/m^3$.

It is therefore obvious that the taking of suitable air samples presents a consider
able problem. Each one of these specifications requires special consideration.

To meet the first requirement, ideally it would be necessary to take a sample c
air over a period of 8 h at a carefully maintained constant flow, collect all the dus
and show that there was less than 2 $\mu g/m^3$ Be present. In practice, however, this i
not usually done, a 4–5 h sample being considered sufficient to give a reasonabl
picture of average atmospheric contamination. A rapid method of analysis is no
essential in this instance.

To meet the second requirement, ideally it would be necessary to have continuousl
recording monitors to register instantaneously any contamination greater tha
25 $\mu g/m^3$. Such a monitor has been described by GILLIESON AND CHURCHILL[3], bu
its reliability has been questioned on the grounds that the response is dependent o
the particle size of the dust, and so an absolute measure of the beryllium concer
tration cannot be obtained. It is moreover, a very expensive instrument. In practic
therefore, a sample is taken over as short a period as possible, bearing in mind th
limit of sensitivity of the analytical method being used. A rapid method of analys
is essential if any action is to be taken as a result of this analysis.

To meet the third requirement ideally, one would take samples of air over th
monthly period and show that the average contamination was less than 0.01 $\mu g/m$
In practice, however, it is usual to take a sample over a period of at least 8 h, passin
about 30–40 m^3 air through the dust collector. If several such samples are below th
limit of 0.01 $\mu g/m^3$ it is reasonable to assume that a monthly average would also b
below that level.

From the above considerations, various assumptions can be made as to the requir
ments of the analytical method.

a. The lower limit of sensitivity required is governed by the third specificatio
(<0.01 $\mu g/m^3$). Since about 30–40 m^3 air are used, a lower limit of about 0.1 μ
beryllium is sufficient to give a margin of about 25–30% of tolerance.

b. The method should be simple and rapid to meet as nearly as possible th
requirements of the second specification (25 $\mu g/m^3$ for a short period). If 1 μg ca
be detected with certainty, then it would be only necessary to sample 0.04 m^3 ai
i.e. for less than 1 min.

c. The method must be highly specific for beryllium, and this is specially importar
to meet the requirements of the third specification, when there will be gross dilutic
of any beryllium by ordinary dust constituents. (This is also an important factor
the analysis of smear samples).

d. The filter used in collecting the dust must:

1. Retain as many as possible of the particles of beryllium-bearing dust in th

article size range 0.5–1.5 μ. These are thought to be of the greatest significance as lung irritant.

2. Pass as fast a flow of gas as is possible, consistent with 1.

3. Not readily clog, as this would make it difficult to maintain a constant flow over a period of several hours.

Airborne dust collection

In most of the analysis so far carried out at Whetstone, samples of dust have been collected by passing air through a 5.5 cm No. 41 Whatman filter paper, at a rate of about 3–4 m³/h using a Fleming Radio (Development) Ltd. Dust Sample Unit Type No. 1355 B. However, No. 41 Whatman filter papers are not ideal media for collecting dust samples. They have several disadvantages.

1. Two investigators[4,5] have shown that particles below 2 μ are not quantitatively retained, and we have confirmed this, (see later).

2. They have a marked tendency to clog up over an extended period, especially in dusty atmospheres.

3. They have certain disadvantages when a rapid method of analysis is required (see later).

They have the advantage of being cheap, readily available, and of having low mineral content.

We have recently investigated Membrane air filters, manufactured by the Membran Filter-gesellschaft, Göttingen, Germany*. These membranes have an extremely fine pore system, and act as mechanical sieves. They are synthetic cellulose-ester materials, and have several properties which make them very useful for air filtration.

a. The pore sizes are carefully controlled so that particles down to any given size can be quantitatively retained.

b. They show a marked resistance to clogging, and in this respect are greatly superior to filter paper.

c. They lend themselves to rapid analysis (see later).

Various porosities were examined, and of those tested AF 400 and AF 600 were the most useful.

The air flow through the filter is an important factor and Table I shows the volumes

TABLE I

COMPARISON OF FLOW-RATES OF VARIOUS FILTERS

Filter medium		Volume of air in 10 min (m³)
Membrane filter	AF 600	1.48
	AF 400	0.65
	AF 150	0.11
Whatman filter paper	No. 41	1.13
	No. 40	0.51
	No. 542	0.12

* Obtainable in Great Britain from Hudes Merchandising Co. London.

of air passed by various filters over a period of 10 min at a constant pressure differ-
ence. This indicates that AF 400 is nearly equivalent to No. 40 paper and AF 600
to No. 41 paper.

However, the position is rather different for tests taken over a longer period, as
Table II shows. It will be seen that a direct comparison between Membrane filter
AF 400 and filter paper No. 41 shows that initially the flow rate through the filter
paper is much faster, but rapidly falls off, and over a period of three hours as much
air is passed by the membrane filter as the filter paper. This is in spite of the fact that
more dust was collected on the membrane filter then on the filter paper, as the
weight of ash indicates.

TABLE II

COMPARISON OF FLOW-RATES OF FILTERS OVER A PERIOD OF TIME

Time	Air passed in m^3 AF 400 membrane	Air passed in m^3 No. 41 paper
30 min	1.7	2.5
1 hour	3.6	4.6
90 min	5.1	6.2
2 hours	6.5	7.4
2½ hours	7.7	8.3
3 hours	8.7	8.9
Weight of ash after 3 hours	4.5 mg	2.8 mg

Some tests carried out on the particle sizes of dust retained by the membrane
filters indicated that the maker's claims (AF 400 retains particles $>0.5 \mu$, and AF 600
retains particles $>1.0 \mu$), were justified. When a No. 41 filter paper was placed in
series with an AF 600 or an AF 400 membrane filter, a considerable number of par-
ticles passed through the filter paper and were retained on the membrane filters.
It was also shown that a small number of particles passed through an AF 600 mem-
brane filter, but were retained on the AF 400 filter. This indicates that the AF
400 filter is the more reliable, but where a fast flow rate is required, as in taking short
duration samples, the AF 600 filter is preferable. It will be seen from the above
consideration that membrane filters are preferable to filter papers on several counts;
their only disadvantage is their relatively high cost.

Possible methods of analysis for beryllium

Several spectrographic methods[6-9], have been described for the determination
of beryllium retained on dust filters. These methods have the advantage of specifi-
city and speed. However, they have a relatively low precision, and if a considerable
number of analyses are required, an expensive piece of apparatus is tied up. For
theses reasons an alternative procedure was investigated.

Fluorimetric methods have been described by several authors[10-13].

However, these depend on an initial partial separation of the beryllium and are
therefore time-consuming. Various spectrophotometric methods have also been
described for the determination of beryllium, using such reagents as p-nitrobenzene-

ᴐ-orcinol, eriochrome cyanine-R, aurine tricarboxylic acid (aluminon), naph-
ᴜzarin, quinalizarin, and naphthachrome Green G. However, various other metals
ᴉerfere with the determination of beryllium using these reagents, including iron,
ᴑalt, aluminium, titanium, zinc, zirconium, copper, vanadium and chromium.
ᴉKE AND CAMPBELL[14] describe the use of aluminon for the determination of beryl-
ᴍ in beryllium copper, where interference due to other metals present in the alloy
ᴉsmall amounts is eliminated by complexing them with ethylenediaminetetracetic
ᴉd. This has been investigated as a possible technique for determining beryllium
ᴉ dust samples. Preliminary experiments with aluminon (after purification by a
ᴐcial technique, described later) indicated that it was a sufficiently sensitive
ᴜgent for the purpose. Using 4-cm cells and a spectrophotometer at 5300 Å, a blank
ᴑution gave an optical density reading of 0.06; with 0.1 μg Be added the reading
ᴉs 0.08; with 0.5 g Be the reading was 0.13; and with 1.0 μg Be the reading was 0.18.
ᴉ each case in 10 ml total volume). Above 8.0 μg Be there is a marked reduction
ᴉsensitivity, due to insufficient reagent being present, (using the quantity described
ᴉer in the appendix). If more reagent is used, the blank reading is correspondingly
ᴇher.

These preliminary experiments led to further investigation and the procedure
ᴉally adopted was a modified "aluminon" method.

ᴇeparation of the sample for analysis

There are two alternative methods of preparing the sample for analysis.
ᴀ. Dry ignition followed by solution of the ash.
ᴉb. Wet acid oxidation.
There is a slight preference for the former method since smaller quantities of rea-
ᴉnts are used, so that the final analysis can be carried out on a small volume without
ᴇ necessity of evaporation. Moreover, there is a possibility that calcined beryllium
ᴉide may be present in the dust, and be insoluble in the acid solvent. In the ignition
ᴑcedure, the filter paper is ignited at 800° in a silica crucible until there is no
ᴦbonaceous material remaining. (In the event of using membrane filters, it is only
ᴉcessary to fold and apply a lighted match followed by a 30-sec ignition to remove
ᴉst traces of organic matter, a far more rapid procedure than for filter papers.) The
ᴉh is fused at 600° with 0.25 g potassium bisulphate to ensure complete solution of
ᴇ beryllium oxide. The melt is extracted with dilute hydrochloric acid — if silica
ᴇcipitates at this stage, it is removed by centrifuging.

ᴉterference due to other metals

All the metals normally found in atmospheric dust were tested for interference in
ᴇ proposed procedure, using EDTA as a complexant. No interference was observed
ᴦ calcium, magnesium, zinc, aluminium, titanium, cobalt, copper, vanadium or
ᴉckel in quantities up to 2 mg. Iron interfered very slightly, as its complex with
ᴑTA absorbed very slightly at 5300 Å. However, compensation for this could very
ᴇsily be made, when appreciable amounts were present, by measuring the absorption
ᴉ 4200 Å and making an appropriate correction (see later).
ᴉZirconium interfered very slightly, 1 mg Zr giving a colour equivalent to 0.6 μg Be,
ᴉile chromium interfered considerably, 0.1 mg Cr giving a colour equivalent to

1.0 μg Be. Use is therefore made of the fact that both these metals form more stabl[
complexes with nitrilotriacetic acid than with EDTA. By addition of this complexant
interference by zirconium is eliminated, and interference by chromium very markedl[
reduced, (0.5 mg Cr gives a colour equivalent to 0.3 μg Be). This can usually b[
neglected since chromium is not normally present in dust. If it should be present i[
would be readily detected since its complex with aluminon is a characteristic mauv[
colour, and a correction could be made by also measuring the absorption at 6000 Å[
where the absorption due to beryllium is negligible, while the absorption due t[
chromium is a little less than at 5300 Å.

Development of the colour complex

To the acid solution of the potassium bisulphate fusion, EDTA and nitrilotriaceti[
acid solution are added, and the pH adjusted to the range of 4–7 with dilute ammonia[
A buffered solution of aluminon is then added (pH 5.8). This pH was found to be th[
most suitable, combining the advantages of a low blank reading with maximun
sensitivity for beryllium. The solution is then diluted to volume, colour developmen[
completed by heating in a boiling water bath for 10 min, the solution cooled and th[
absorption measured at 5300 Å. After a little experience, it is possible to estimate th[
approximate beryllium level by visible inspection immediately after adding th[
aluminon reagent, if a rapid "safety" check is required.

Time of analysis

Normally one analysis can be completed in 30 min after taking the sample, or fou[
analyses in 45 min. However, this can be speeded up if an approximate figure i[
acceptable. A dust sample can be collected on an AH 600 membrane filter ove[
5 min taken to the laboratory ignited and fused with bisulphate in 2 min, coole[
extracted with dilute acid in 2–3 min, and the colour developed in the cold an[
estimated visually in 2–3 min; a total time of about 15 min, or 7 min after th[
sample has been received in the laboratory.

Precision

In checking the method, several dust samples were collected from different locali[
ties; in each case the dust filter was divided exactly in two, and a known amount o[
standard beryllium solution added to one of the two halves. The two halves wer[
then analysed separately for beryllium. Recoveries in all cases were between 90–
105% at the 0.5 to 5 μg level. Below 0.5 μg the accuracy falls off, but the lower limi[
is estimated to be 0.1 μg, where there is an O.D. difference of 0.02 from the blank
(The blank on one particular batch of reagent does not vary more than $\pm$ 0.00[
O.D.).

Use of method

At the time this paper was written, over 500 samples had been analysed, with
beryllium contents ranging from <0.1 μg (over 50%) up to 20 μg. Only a very smal[
minority (less than 3%) have been outside the tolerance level laid down; and with
one exception these have all been surface samples.

gents

.. Complexing solution: Dissolve 8 g EDTA (disodium salt) and 2 g nitrilotriacetic acid in 80 ml
er, adding ammonia dropwise to neutralise the free acid, and dilute to 100 ml.
. Aluminon reagent: Aluminon is first purified as follows: Dissolve 2 g aluminon in 400 ml
er and add 4 ml hydrochloric acid. Transfer to a separating funnel, add 500 ml ether and
ract the aurine tricarboxylic acid. Filter the ether extract through a dry filter paper, and back
ract the aluminon with 400 ml 0.5% ammonia. Run off the aqueous layer and dilute to 1 l.
ake 800 ml of this solution, add 200 g ammonium acetate and 20 ml acetic acid dissolved in
ml water. Add 1.2 g benzoic acid dissolved in 4 ml methanol, then add 400 ml 1% gelatin
tion (polarographic grade). Adjust the pH to 5.8. Finally dilute to 2 l and store in a dark
tle.
. Dilute ammonia 30%.

samples

gnite the filter containing the dust sample at 800° until no carbon remains (if a
mbrane filter has been used, first ignite by applying a lighted match). Cool slightly,
d about 0.25 g potassium bisulphate and fuse at about 600° for 1–2 min (the ash
uld yield a clear melt; if necessary add a little more KHSO$_4$). Cool, and extract
melt with 3 drops hydrochloric acid and about 3 ml water. If silica is present,
trifuge at this stage. Add from a polythene dropping bottle 10 drops of complexing
ution, and dilute ammonia dropwise until the pH is in the range 4–7, (*Note a*) add
l buffered aluminon solution and dilute to 10 ml in a graduated flask. Immerse
flask for 10 min in a boiling water bath, cool, and measure the absorption in a
m cell at 5300 Å. This covers the range 0–8 μg Be. (*Note b*).

te a

If there is an appreciable yellow coloration before adding the aluminon, due to
n, it is necessary to make a correction. To do this, measure the optical density of
final solution at 4200 Å and divide the figure by 30. Subtract this figure from the
D. at 5300 Å to obtain the corrected beryllium reading.

te b

If the reading indicates that more than 8 μg Be is present, take 5 ml of the final
ution, add another 4 ml aluminon reagent, another 20 drops of complexing reagent,
ute to 25 ml and heat for a further 10 min; cool and measure as before. This extends
range to 25 μg Be, and if necessary a further dilution could be carried out in a
milar manner.

near samples

These are treated in a similar manner to air samples but as they usually contain
ore total inorganic material, double the quantities of reagents used throughout and
lute the final solution to 20 ml.

alibration

A calibration graph is prepared using the above procedure for air samples. A master
andard beryllium solution is prepared by dissolving 0.1 g beryllium metal in 80 ml
% hydrochloric acid under reflux and diluting to 100 ml. 1 ml of this solution is then
luted to 1000 ml to give a solution containing 1 μg beryllium per ml. Aliquots of

0, 0.5, 1, 2, 3, 4, 6 and 8 ml of this solution are taken to cover the range 0–8 μg Be
A separate calibration graph is required for smear samples over the range 0–16 μg Be
It is essential to prepare fresh calibration graphs for each batch of reagent.

Conclusion

This method can be regarded as a satisfactory alternative to the spectrographi
method, in the determination of beryllium for monitoring purposes.

SUMMARY

The requirements of beryllium monitoring are discussed. Emphasis is placed on developin
an analytical procedure which is rapid, simple to operate, of adequate sensitivity and of reasonabl
accuracy. For air analysis, beryllium bearing dust is collected on a membrane filter, the berylliu
is obtained in solution and determined spectrophotometrically, using aurine tricarboxylic aci
(aluminon) as reagent. Interference due to other metals is avoided by the addition of suitabl
complexing agents. A sensitivity of 0.1 μg Be can be achieved.

RÉSUMÉ

L'auteur a mis au point une méthode de dosage du glucinium dans l'air et dans les poussières
Il s'agit d'une méthode spectrophotométrique, utilisant l'acide aurinetricarboxylique (aluminon
comme réactif.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Beryllium i
der Atmosphäre und in Staub. Als Reagenz dient Aurintricarbonsäure (Aluminon).

REFERENCES

1. R. O. R. BROOKS, *Nuclear Power*, 3 (1958) 549.
2. D. W. WHITE, JR. AND J. E. BURKE, "*The Metal Beryllium*", American Society for Metals
   Cleveland, Ohio 1955.
3. A. C. H. P. GILLIESON AND W. L. CHURCHILL, *Spectrochim. Acta*, 5 (1952) 238.
4. C. N. DAVIES, *Brit. J. Ind. Med.*, 6 (1949) 245.
5. J. FITZGERALD AND C. DETWILER, *U.S.A.E.C. Rept. KAPL*, 1463 (1955).
6. W. J. SMITH AND N. F. SURPRENANT, *Proc. A.S.T.M.*, 53 (1953) 1122.
7. J. CHOLEK AND D. M. HUBBARD, *Anal. Chem.*, 20 (1948) 73, 970.
8. F. T. BIRKS, *A.E.R.E. Rept, C/R*, 1952 (1956).
9. F. P. LANDIS AND M. C. COORS, *Appl. Spectroscopy*, 8 (1954) 71.
10. T. Y. TORIBARA AND R. E. SHERMAN, *Anal. Chem.*, 25 (1953) 1594.
11. M. ISHIBASHI, T. SHIGEMATSU AND Y. NISHIKAWA, *Bull. Inst. Chem. Research. Kyoto Univ.*, 3
    (1956) 210.
12. J. M. RILEY, *U. S. Bur. Mines, Rept. Invest.*, No. 5282 (1956).
13. C. W. SILL AND C. P. WILLIS, *Anal. Chem.*, 31 (1959) 598.
14. C. L. LUKE AND M. E. CAMPBELL, *Anal. Chem.*, 24 (1952) 1056.

POTENTIOMETRIC DETERMINATION OF MERCURY(II) WITH ETHYLENEDIAMINETETRAACETIC ACID

ANALYSIS OF BINARY MIXTURES

H. KHALIFA AND M. G. ALLAM

Analytical Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt (U.A.R.)

REILLY AND PORTERFIELD[1] has shown that mercuric nitrate can be used for the
complexometric backtitration of excess ethylenediaminetetraacetic acid (EDTA) in the
determination of many metals. KHALIFA[2] *et al.* later showed that the Hg/HgY^{-2} system
could be successfully applied for the same purpose. A silver amalgam electrode was
immersed in a solution of the metal complexan which contained excess EDTA and
was buffered to pH 8–11 with ammonium hydroxide and nitrate; a saturated
calomel electrode and 0.05 M $Hg(NO_3)_2$ solution were used.

The cells and the potentials at the beginning of the titration and at 0.1 ml of titrant
after the end-point may be represented as:

	pH	8	9	10	11
Ag/Hg^{-2} KNO$_3$ – KCl Hg$_2$Cl$_2$/Hg	mV	216	171	126	76
Ag/[Hg(NH$_3$)$_2$]$^{+2}$ KNO$_3$ – KCl Hg$_2$Cl$_2$/Hg	mV	326	286	240	191

This method permitted detection of the end-point with reasonable accuracy and
several metals could be determined.

The aim of the present work was to develop a simple, rapid and accurate method
for the determination of milli- and microgram amounts of mercury(II).

Comparatively little work has been done on the titrimetric determination of mer-
cury with EDTA. (The gravimetric sulphide method is time-consuming and is not
suitable for micro amounts of mercury.) Mercury(II) has been determined by direct
titration with EDTA in presence of xylenol orange indicator[3], and indirectly with
excess of EDTA and back-titration with magnesium or zinc solution in presence of
Eriochrome Black T indicator[4].

A potentiometric procedure has the certain advantage that no interference with
the colour change of the indicator occurs when mercury has to be determined in,
for example, pharmaceutical products. A potentiometric method with potassium
iodide as titrant and platinum amalgam as the indicator electrode[5] can be used to
determine 0.5 to 70 mg of mercury. The present method permits the determination of
0.2 to 100 mg of mercury(II) with reasonable accuracy.

EXPERIMENTAL

Reagents

Twice-distilled water was used for all solutions. The materials were the most pure available. The metals were used generally in the form of their nitrates.

Solutions

Mercuric nitrate solution was prepared by dissolving 9.0577 g of the analytical grade reagent (Mallinckrodt) in 500 ml water with the addition of a minimum amount of conc. nitric acid (*ca.* 4 ml). The solution was standardised either gravimetrically as sulphide or volumetrically by back titration of excess EDTA with a standard magnesium solution using Eriochrome Black T as indicator. Both methods gave the same result, *i.e.* 20.38 mg of mercury(II) per ml. Further dilutions were prepared from this stock solution.

EDTA solutions (0.05 to 0.005 M), were prepared and standardised in the usual manner.

Aluminium solution was prepared and standardised as previously described[6] from potassium aluminium sulphate. Other metallic solutions (except those mentioned below) were prepared in the usual way and standardised according to the procedures of SCHWARZENBACH[7]; the solutions were 0.01 to 0.03 M and all were made slightly acidic in nitric acid.

Manganous solution was prepared from AR manganous sulphate by dissolving 2.2306 g in water, adding 2 ml of 9 N sulphuric acid solution and diluting to 500 ml with water. This solution was standardised according to FLASCHKA[8], excess EDTA being back-titrated with magnesium solution after addition of tartaric and ascorbic acids.

Zinc solution was prepared from AR zinc oxide by dissolving 0.8138 g in the minimum amount of 1 : 1 nitric acid and diluting to 500 ml with water; the solution was found to be 0.02005 M

Buffer solutions (pH 8 to 11) were prepared and standardised as previously described. The pH values were checked with a hydrogen electrode. The titration apparatus and the potentiometer were essentially similar to those described previously[9].

PROCEDURES

Mercury alone was determined by titrating different volumes of buffered mercury solutions with EDTA solutions using the silver amalgam electrode to detect the end-points. Reverse titrations were also carried out.

The procedure for the analysis of binary mixtures of mercury and barium was based on the use of selective pH. Binary mixtures of mercury and aluminium were analysed with the help of masking agents such as triethanolamine or ammonium fluoride. Binary mixtures of mercury with any of the other cations mentioned were analysed by two potentiometric titrations; one gave the content of mercury and the other the content of mercury plus the other metal. In some cases mercury was masked with potassium iodide and the other cation was titrated with EDTA using a suitable buffer and indicator.

RESULTS

The molarity (0.1016) of the stock mercury solution was checked by titrating 2.5-, 5- and 7.5-ml portions of 0.04 M EDTA at pH values 8, 9 and 10; the inflexions near the end-point were 90–106 mV per 0.1 ml of titrant. When 1-, 2- and 3-ml portions of the same mercury solution were titrated with 0.04 M EDTA at pH 8 or 9, the inflection averaged 70 mV per 0.1 ml of titrant. The average molarity of the mercury solution from these titrations was 0.1016 which agrees well with the previous figure of 20.38 mg of mercury per ml.

The results obtained with 0.05, 0.02 and 0.01 M Hg or EDTA solutions are listed in Table I.

These results and some of the corresponding curves (Fig. 1) show that mercury

TABLE I

	Hg taken mg	Hg found mg EDTA titrated with Hg	error %	Hg found mg Hg titrated with EDTA	error %	mV/0.1 ml Hg or EDTA
0.05 M Hg and EDTA						
pH 8	20.06	20.13	+0.36	20.01	—0.26	72
	30.09	30.19	+0.32	30.04	—0.20	71
	40.12	40.26	+0.36	40.07	—0.12	72
pH 9	20.06	20.16	+0.50	20.16	+0.50	85
	30.09	30.19	+0.32	30.19	+0.32	88
	40.12	40.26	+0.36	40.04	—0.20	86
pH 10	20.06	20.12	+0.30	20.06	0.00	93
	30.09	30.19	+0.32	30.04	—0.17	97
	40.12	40.26	+0.36	40.04	—0.20	94
0.02 M Hg and EDTA						
pH 8	8.02	8.02	0.00	8.02	0.00	65
	12.04	12.07	+0.30	11.99	—0.35	60
	16.05	16.09	+0.24	15.97	—0.50	60
pH 9	8.02	8.05	+0.35	7.99	—0.45	77
	12.04	12.03	—0.03	12.08	+0.35	79
	16.05	16.02	—0.20	16.02	—0.20	75
pH 10	8.02	8.06	+0.50	8.05	+0.35	86
	12.04	12.08	+0.40	11.99	—0.35	85
	16.05	16.11	+0.40	16.02	—0.20	81
0.01 M Hg and EDTA						
pH 8	4.01	4.03	+0.49	3.99	—0.49	55
	6.02	6.02	0.00	5.98	—0.70	52
	8.02	8.02	0.00	7.96	—0.80	51
pH 9	4.01	4.01	0.00	4.03	+0.49	60
	6.02	6.00	—0.30	5.99	—0.50	61
	8.02	8.00	—0.30	7.94	—1.00	60
pH 10	4.01	4.05	+1.00	4.05	+1.00	70
	6.02	6.06	+0.70	5.99	—0.50	71
	8.02	8.05	+0.30	7.94	—1.00	69

TABLE II

ANALYSIS OF MIXTURES OF MERCURY AND ALUMINIUM

Hg taken mg	Hg found mg	error %	Al taken mg	Al found mg	error %
0.0434 M Hg + 0.1906 M Al with 0.02 M EDTA and 0.0434 M Hg(NO₃)₂ solutions.					
4.353	4.370	+0.39	2.573	2.568	—0.19
8.706	8.741	+0.42	5.146	5.158	+0.23
8.706	8.702	—0.05	2.573	2.576	+0.12
0.0283 M Hg + 0.0382 M Al with 0.0202 M EDTA and 0.0283 M Hg(NO₃)₂ solutions.					
2.838	2.838	0.00	0.512	0.511	—0.19
5.677	5.469	—0.49	1.025	1.020	—0.49

(4 to 40 mg) can be determined with reasonable accuracy; reasonable potenti
jumps of from 50 to 97 mV per 0.1 ml of titrant are given at the end-point.

Below 0.01 M the results were about 2% low; better results were obtained bel
pH 9. At pH 8 and especially when smaller amounts of the buffer were used the er
was less than 2%. It was found that buffer pH 6 (KH$_2$PO$_4$–NaOH) was best for t
titration of 0.005 M mercury or 0.005 M EDTA in either direction. The results, whi
involved negligible errors, are shown in Fig. 2. It is possible to determine 200 μg
mercury(II) without difficulty.
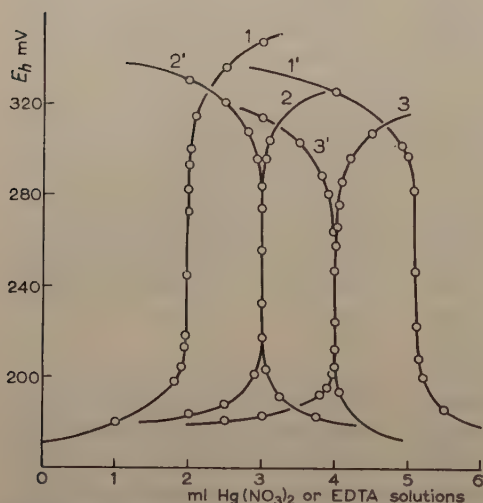
Fig. 1. Titration curves of EDTA against mer-
curic solution or vice versa, at pH 9. 1. 5 ml 0.04 M
EDTA with 0.1016 M Hg solution. 1'. 2 ml 0.1016
M Hg with 0.04 M EDTA solution. 2. 3 ml 0.05 M
EDTA with 0.05 M Hg solution. 2'. 3 ml 0.05 M
Hg with 0.05 M EDTA solution. 3. 4 ml 0.02 M
EDTA with 0.02 M Hg solution. 3'. 4 ml 0.02 M
Hg with 0.02 M EDTA solution.
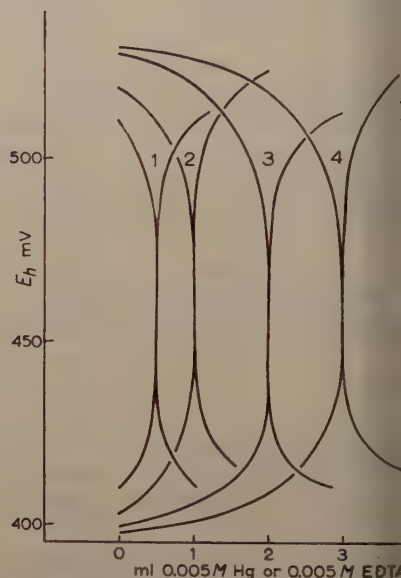
Fig. 2. Titration curves of EDTA again
mercuric solution or vice versa. 1. 0.5
of 0.005 M Hg with 0.005 M EDTA
vice versa. 2. 1 ml of 0.005 M Hg wi
0.005 M EDTA or vice versa. 3. 2 ml
0.005 M Hg with 0.005 M EDTA or vi
versa. 4. 3 ml of 0.005 M Hg with 0.005
EDTA or vice versa.

*Analysis of binary mixtures of mercury with some other metals by the use of maski
agents*[10]

Triethanolamine forms stable complexes with iron, aluminium and manganes
The aluminium couplex formed in ammoniacal solution serves to mask this meta
Fluoride forms stable complexes with aluminium, iron, titanium and beryllium an
precipitates the alkaline earth metals. KHALIFA et al.[2] have studied the effect
triethanolamine, tartrate, citrate, sulphate and chloride on the titration of EDT
with mercury(II); they found that only appreciable amounts of chloride should
absent. Ammonium fluoride was examined as a masking agent in this investigatio
buffered mercury or EDTA solutions were made 0.1 M in fluoride before titratio
Fluoride ion had no effect over the whole range of pH except to improve the end-poi

ction at pH 8 when EDTA was titrated with mercury. When the above-mentioned
ons were masked by triethanolamine or ammonium fluoride, it was concluded that
monium fluoride was preferable to triethanolamine. We also analysed mixtures
ercury and aluminium by adding excess EDTA and back-titrating with mercuric
ate solution with and without fluoride present. In absence of fluoride, both metals
titrated and the aluminium was found by difference. Representative results are
n in Table II.

pride has also been used to mask lanthanum in the analysis of mixtures of mer-
and lanthanum[11].

lysis of mixtures of mercury and barium by means of selective pH[12]

xcess of EDTA was added and back-titrated at pH 8 (which gave the EDTA
valent to mercury only) and at pH 10.5–11 (which gave both mercury and
um). Representative results are shown in Table III.

TABLE III

Analysis of 0.0504 M Hg + 0.05 M Ba

Hg taken mg	Hg found mg	error %	Ba taken mg	Ba found mg	error %
6.868	6.923	+0.81	5.056	5.075	+0.38
5.494	5.915	+0.45	10.112	10.120	+0.08
3.434	3.447	+0.38	5.056	5.051	—0.10

lysis of binary mixtures of mercury with lead, manganese or zinc

wo methods were used. One involved the potentiometric titration of mercury
presence of the other cation with potassium iodide solution using silver amalgam as
icator electrode; both cations were then determined by potentiometric back-
ation of excess EDTA with mercuric nitrate solution.

he other procedure involved the potentiometric titration of mercury(II) or the
al content of the mixture as mentioned above; the other cation was then deter-
ned while mercury was masked with potassium iodide.

n the case of mercury and lead, lead was determined by adding a few crystals of
taric acid, excess of potassium iodide (to form potassium mercuric iodide) and
ml of NH₄OH – NH₄NO₃ buffer pH 9, and titrating with 0.02 M EDTA using
ochrome black T as indicator. With mercury and zinc both the above methods gave
isfactory results in the presence or absence of potassium thiocyanate. When
assium thiocyanate (0.5 ml of 0.2 M solution per 1 ml of 0.01 M mercury(II)
ution) was present equilibrium was attained only after 5 min near the end-point.
e maximum inflection per 0.1 ml of 0.0101 M potassium iodide solution averaged
mV whereas it averaged 265 mV in the absence of thiocyanate. Such procedures
be used to analyse zinc mercuric thiocyanate. In the case of mercury and manga-
se, potassium iodide (0.5 ml of 0.1 M solution per 1 ml of 0.01 M Hg solution),
orbic acid (0.2 ml of 0.1 M solution per 1 ml of 0.0268 M manganese(II) solution),
taric acid and buffer pH 9 were added before titration of manganese(II) with EDTA
ution; the sum of the metals was then determined by potentiometric back-titration

TABLE IV

Analysis of Hg (0.009 M) + Pb (0.010 M) or Mn (0.0268 M) or Zn (0.0201 M)

Volume ml		ml 0.02 M EDTA	Molarity of metal	Molarity of Hg direct titration	mV per 0.1 ml 0.0101 M KI	Molarity of Hg back-titration
4Hg + 2	Pb	0.990	0.00990	0.009027	267	0.00900
3Hg + 1	Pb	0.495	0.00990	0.009005	244	0.00903
2Hg + 3	Pb	1.490	0.00993	0.008960	293	0.00898
1Hg + 0.5	Pb	0.250	0.01000	0.008963	315	0.00895
4Hg + 2	Mn	2.680	0.02680	0.009019	206	0.00898
3Hg + 1	Mn	1.345	0.02690	0.009001	208	0.00899
2Hg + 3	Mn	4.020	0.02680	0.008989	300	0.00905
1Hg + 0.5	Mn	0.670	0.02680	0.008938	280	0.00904
4Hg + 2	Zn	2.010	0.02010	0.008950	70	0.00901
3Hg + 1	Zn	1.000	0.02000	0.009040	98	0.00901
2Hg + 3	Zn	3.020	0.02013	0.008950	99	0.00896
1Hg + 0.5	Zn	0.500	0.02000	0.009020	104	0.00888

of EDTA, the mercury being determined by difference. Representative results are listed in Table IV.

Analysis of binary mixtures of mercury(II) with nickel, cadmium or cobalt

Mercury(II) was titrated with potassium iodide and the total metals were determined by back-titration with mercuric nitrate, the other metal being determined by difference. Representative results are shown in Table V.

TABLE V

Analysis of Hg (0.010 M) + Ni (0.0201 M), Co (0.0200 M) or Cd (0.0201 M)

Hg taken mg	Metal taken mg		Hg found by KI mg	error %	Metal found mg		error %
8.024	2.359	Ni	8.088	+0.79	2.364	Ni	+0.21
6.018	1.180	Ni	6.028	+0.16	1.183	Ni	+0.17
4.012	3.538	Ni	3.999	−0.32	3.560	Ni	+0.62
2.006	0.590	Ni	1.996	−0.49	0.590	Ni	+0.00
8.024	4.496	Cd	8.053	+0.36	4.489	Cd	−0.15
6.018	2.248	Cd	6.047	+0.48	2.248	Cd	0.00
4.012	6.745	Cd	4.000	−0.30	6.740	Cd	−0.07
2.006	1.124	Cd	2.011	+0.25	1.124	Cd	0.00
8.024	2.369	Co	8.072	+0.59	2.369	Co	0.00
6.018	1.185	Co	6.054	+0.59	1.179	Co	−0.51
4.012	3.554	Co	3.992	−0.49	3.571	Co	+0.48
2.006	0.592	Co	2.011	+0.24	0.592	Co	0.00

The above data show that the procedure described is simple and suitable for the determination of many binary mixtures containing mercury(II). Furthermore, it can be modified for the analysis of mixtures of mercury with more than one cation.

SUMMARY

Potentiometric determination of mercury(II) with EDTA using silver amalgam as indicator electrode, is suitable for 200 μg to 100 mg of mercury. Binary mixtures of mercury(II) with other metals can be analysed by different methods involving masking agents, selective pH and differential titrations.

RÉSUMÉ

e méthode potentiométrique est proposée pour le dosage du mercure(II) au moyen de l'acide
ylènediaminotétracétique en présence d'amalgame d'argent comme électrode indicatrice. Des
thodes sont également proposées pour l'analyse de mélanges binaires du mercure(II) avec
utres métaux.

ZUSAMMENFASSUNG

wird eine Methode beschrieben zur potentiometrischen Bestimmung von Quecksilber(II) mit
hylendiaminotetraessigsäure und Silberamalgam als Referenzelektrode. Die Methode lässt
n auch zur Analyse binärer Gemische von Quecksilber(II) mit anderen Metallen verwenden.

REFERENCES

C. N. REILLY AND W. W. PORTERFIELD, *Anal. Chem.*, 28 (1956) 443.
H. KHALIFA, R. PATZAK AND J. DOPPLER, *Z. anal. Chem.*, 161 (1958) 264.
J. KÖRBL AND R. PRIPIL, *Chemist Analyst*, 45 (1956) 102.
W. BIEDERMANN AND G. SCHWARZENBACH, *Chimia Switz*, 2 (1948) 56; *C.A.*, 44 (1950) 9596.
T. SALEM, *Inst. D'Egypt*, 2 (1956) 38.
H. KHALIFA, *Z. anal. Chem.*, 163 (1958) 81.
G. SCHWARZENBACH, *Complexometric titrations*, Methuen & Co. Ltd, London; Interscience
  Publishers Inc., New York 1957.
H. FLASCHKA, *Chemist Analyst*, 42 (1953) 56; *C.A.*, 47 (1953) 10637.
H. KHALIFA, *Z. anal. Chem.*, 161 (1958) 401.
F. J. WELCHER, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand
  Company Inc., Toronto, New York and London, 1957, p. 72.
H. KHALIFA, M. HAMDY AND A. SOLIMAN, *Z. anal. Chem.*, in the press.
H. KHALIFA, *Anal. Chim. Acta*, 18 (1958) 310; *Z. anal. Chem.*, 159 (1958) 410, 165 (1959) 138.

RAPID METHOD FOR THE DETERMINATION OF FLUORIDE
IN LIQUIDS

S. A. BARTKIEWICZ AND J. W. ROBINSON

so Research Laboratories, Esso Standard Oil Company, Louisiana Division, Baton Rouge, La.
(U.S.A.)

DISCUSSION

he determination of fluoride always presents a problem in sample handling.
tandard ashing procedures depend on the volatilization of the fluoride. This is
ecause it easily forms the volatile compounds HF and SiF_4. This property has, of
ourse, provided the base for many successful separation procedures. Techniques
nvolving the use of bombs have also been used successfully. At best, however, these
rocedures are tedious, time-consuming and require close attention. Also, a serious
mitation of bomb techniques is that the sample size is limited. For trace fluoride
etermination (less than 100 p.p.m.) this is a severe handicap.

Other procedures which have recently been applied successfully to this analysis
nclude the SHÖNIGER flask technique[1] and the use of the WICKBOLD oxy–hydrogen
urner[2-4].

The SHÖNIGER flask technique had the appeal of simplicity and high speed, but th
small sample size restricts the lower limit of fluorine determinable. The WICKBOL
burner[2,3] has been successfully used for the determination of halides and sulfur i
liquids and gases, and a modification[4] of the WICKBOLD burner has been made t
enable solids samples to be analyzed. But again the sample size is limited by th
capacity of the combustion boat used to contain the sample during the decompositio
stage.
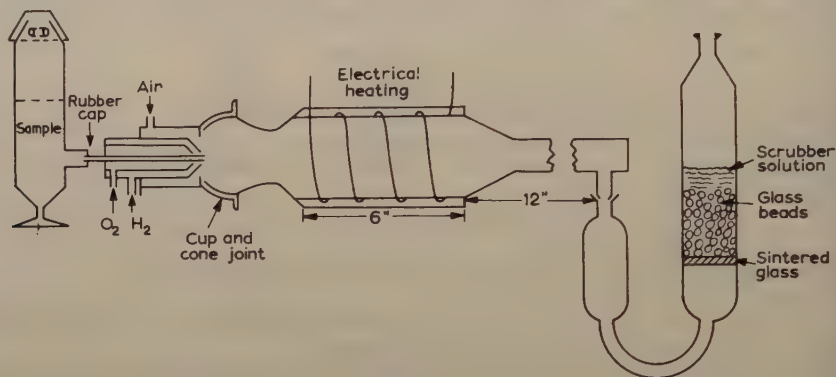
Fig. 1.

The present procedure eliminates the problem of sample size to a considerabl
degree. Any amount of sample can be burned; also, the separation step is simpl
rapid, and requires the minimum of attention.

Apparatus

Furnace. The furnace (Fig. 1) is made of Vicor. It is fitted with a glass 35/25 male ball joint a
one end for attaching the burner, and a male joint at the other end to attach the scrubber.

The first portion of the tube is electrically heated to act as an igniter for the flame. This portio
of the furnace is somewhat wider than the rest of the tube to allow for expansion of the ho
combusting gas.

Scrubber. The scrubber is a standard sintered glass scrubber with glass beads added to gi
better contacting between scrubber solution and combustion products.
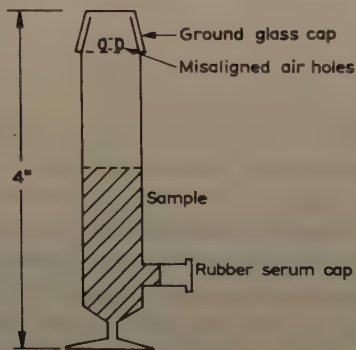
Fig. 2.

Sample container (Fig. 2) This is a glass tube fitted with an open-end side-arm near the bas
A rubber serum cap is placed over this side arm. A ground glass cap is placed on top. A small ho

illed in the cap, and a similar hole is drilled through the container. When sample is being run,
e holes are made to coincide by turning the cap to allow air to pass. At other times, the holes
not coincide. This prevents loss of sample by evaporation.
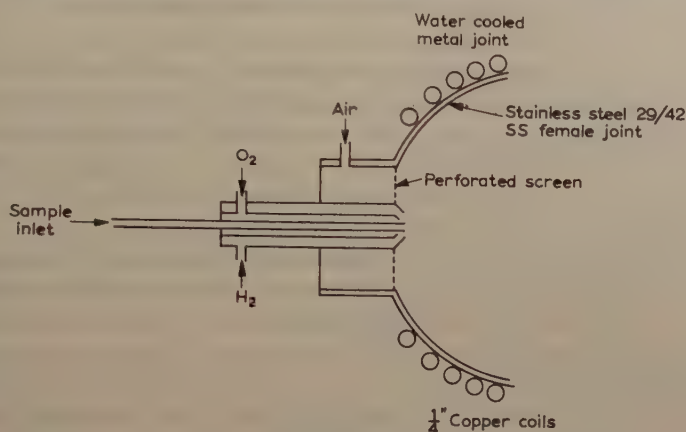
Fig. 3.

Burner (Fig. 3). The burner consists of a Beckman oxy–hydrogen burner brazed into a
ndard 35/25 stainless steel female joint. Space is left for a current of air. The burner is water-
led to prevent overheating.

PROCEDURE

niting furnace

The furnace is heated up to red heat (600°). Oxygen pressure is raised to 3–5 psig
the burner. Hydrogen pressure is increased to 0.5 psig. Under these conditions,
mediate ignition should take place. If it fails to ignite, shut off the hydrogen, then
e oxygen, increase the furnace temperature and repeat the operation.

After ignition, the electrical heating should be turned off to prevent overheating
e glassware. The oxygen and hydrogen pressures are adjusted to 10 and 1.5 psig,
spectively. An air flow of 10–15 l/min is satisfactory.

mple burning

The sample is poured into the sample container and weighed. After the furnace is
nited, the container is then attached to the burner by piercing the serum cap with
e burner inlet capillary (Fig. 1). The air inlet holes in the cap are lined up to allow
ee flow of the sample. Control of feed rate is maintained by misaligning these holes.
is control can be exercised during combustion of sample if necessary.

When sufficient sample has been burned, the sample container is removed and
weighed, the inlet holes being closed. The weight of sample burned is the difference
weight between the container and liquid before and after burning. For samples
ntaining 100 p.p.m. F, 15 g is adequate.

uoride determination

The fluoride in the scrubber may be determined by any conventional method.
e thorium nitrate procedure was used for the work reported in this paper[5]. At-
mpts to use the polarographic procedure[6] required excessive attention. This was
esumably because any error in determining the complexed iron gives a six-fold
crease in error for the fluoride analysis.

Use of 3-amino-methyl alizarin N-N-diacetic acid

Some preliminary studies were made on the use of 3-amino-methyl alizarin N-N-diacetic acid[7] as a colorimetric method for determining fluoride.

It was found that a good calibration curve was obtained over the concentration range 0–10 p.p.m. F. With concentration of fluoride greater than this, the color was bleached out. This concentration range is too limited for applications in the petroleum industry where the fluoride level can vary considerably. Further studies also showed that many metals interferred with the color formation if present in concentrations of 100 p.p.m. or greater. No studies were made below this concentration. These metals included aluminum, iron, nickel, vanadium, boron and copper.

It is believed that the color body in this reaction is a fluoro–cerium-organic addend complex, the formula for which is not yet known. Other metals can interfere in two possible ways: (a) by complexing the fluoride and preventing the formation of the color body, or (b) by forming a more stable color body in which the cerium is replaced by the interfering metal.

Spectrophotometric studies of the solution formed when interfering metals were present revealed that the wavelength of absorption shifted to the near IR or UV. This suggested that the metals were interfering by mechanism (b) and that the metal complex was not destroyed but modified.

Based on this observation, it seems possible that a metal producing a more stable metal fluoro–organo complex than cerium could be used for this reagent. Such a reagent would naturally be less troubled by metal interferences. Although the procedure would of necessity be instrumental, and therefore not applicable to visual qualitative analysis, it would still find a wide application in quantitative analysis.

Unfortunately, the present reagent is troubled by metal interferences, and since these metals are not eliminated in the combustion step, it was decided that this reagent was not generally suitable for application to petroleum fractions, except where the fluoride level and the metal concentrations are very low.

RESULTS

The results obtained using the combustion technique described and normal thorium nitrate finishing technique indicated that the method was rapid (20 min per analysis) and reasonably precise. Accurate results were obtained by burning two compounds which are normally difficult to decompose. Results are listed in Table I.

TABLE I

Compound	Fluoride		% Recovery
	Added (mg)	Recovered (mg)	
Pentafluoropropyl alcohol	18.4	16.4	89
	26.1	22.3	86
Hexafluorodichlorocyclopentane	39.8	37.8	95
	26.4	25.6	97
	27.8	26.4	97
	26.2	24.9	95
	29.8	27.5	93
	6.1	5.8	95
	5.4	5.1	95
	7.7	7.1	92

These results indicated that the type of fluorine analyzed affected the efficiency of composition. Most fluoro compounds are easier to decompose than these and presumably in these cases the per cent recovery would be improved.

SUMMARY

A rapid procedure has been developed for the determination of total fluoride in liquids. The samples are burned in a modified BECKMAN oxy–hydrogen burner. The fluoride is scrubbed out of the products of combustion and determined in any conventional manner.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des fluorures dans des liquides. On procède par combustion; on peut ensuite appliquer l'un des méthodes habituelles pour le dosage du fluorure.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur raschen Bestimmung von Fluoriden in Flüssigkeiten. Die Substanz wird in einer Sauerstoff–Wasserstofflamme verbrannt und das Fluor nach einer der bekannten Methoden bestimmt.

REFERENCES

B. Z. SENKOWSKI, E. G. WOLLISH AND E. G. E. SHAFER, Anal. Chem., 31 (1959) 1574.
R. WICKBOLD, Angew. Chem., 69 (1957) 530.
P. B. SWEETSER, Anal. Chem., 28 (1956) 1766.
D. C. HOEL, D. T. FANALE AND R. O. CLARK, API Meeting, New York, May 1959.
R. BELCHER, S. J. CLARK AND E. CALDAS, Mikrochim. Acta, 3 (1953) 283.
C. E. SHOEMAKER, Anal. Chem., 27 (1955) 552.
R. BELCHER, M. A. LEONARD AND T. S. WEST, Talanta, 2 (1959) 92.

CONTROLLED POTENTIAL ELECTROLYTIC DETERMINATION OF COPPER IN LEAD AND TIN–BASE ALLOYS

B. ALFONSI

Research and Control Laboratory, Auto-Avio, Fiat, Torino (Italy)

(Received June 9th, 1959)

Copper determinations in lead and tin–base alloys can be carried out by electrolytic, iodometric or photometric methods. Generally, these methods require the preliminary separation of copper as sulphide[1], or by salicylaldoxime[2], or the separation of tin and antimony as oxides[3]. More often tin and antimony are volatilized as bromides, lead is separated as sulphate, and then the copper is determined by constant current electrolysis[4]. In the case of tin–base alloys, the electrolysis can be carried out directly

after dissolution in nitric–hydrofluoric acid, but the method has some limitations[4,5]

The two methods described here allow the determination of copper directly from the acid-dissolved alloy by controlled potential electrolysis; this advantageous analytical technique is excellently described by LINGANE[6] who also gives a complete bibliography. In lead–base alloys with a high percentage of antimony, double electrolysis may be necessary.

In tin–base alloys also, the lead may be determined along with the copper; for these alloys, the method is similar to another described previously[7] which was derived from LINGANE's method[6,8]. Here, it is extended to a 5-g sample in order to determine the lead (often present in small amounts) up to a percentage of 0.2%. For lead–base alloys the analysis is also carried out on a 5-g sample because the percentage of copper is generally low. Percentages lower than 0.2% can be better evaluated by photometric or spectrographic methods.

Reagents

Concentrated hydrochloric acid ($d = 1.18$). Concentrated nitric acid ($d = 1.38$). Concentrated ammonia ($d = 0.88$).

Nitro–fluoboric mixture: in a polythene bottle, saturate 40% hydrofluoric acid with boric acid, filter and dilute the filtrate with an equal volume of dilute HNO_3 (1 + 1); keep in a polythene bottle.

Wash solution: distilled water containing one drop of concentrated ammonia per liter.

I. LEAD–BASE ALLOYS

(1) *Antimony:* up to but not more than 1.5%.

Method of analysis

In a 400-ml beaker weigh 5 g of alloy in thin chips, add 20 g of tartaric acid, then 50 ml of distilled water and shake to dissolve the tartaric acid. Add 50 ml of the nitro–fluoboric mixture, cover with a watch glass and heat slightly until all the alloy has dissolved, except for a black residue consisting predominantly of copper which also remains in suspension in the form of flakes. Heat a little more; after a while the dissolution of the residue begins and nitrous vapours develop. The reaction is rather violent and the beaker should be removed from the heating plate to prevent overflowing of the liquid.

This rather violent reaction dissolves all the copper and, when it stops, all the alloy should be dissolved. However, if, on account of excessive heating, violent dissolution of copper starts before all the other metals are completely dissolved, some of the alloy may remain undissolved; if so, the solution should be heated moderately to obtain complete dissolution. In the meantime, however, some tin may precipitate and, in this case, the analysis must be started again from the beginning.

When the dissolution is complete, add, little by little, 4–5 g of urea and immediately wash the watch-glass and the beaker wall with some distilled water, then add 20 ml of 60% perchloric acid and dilute with distilled water. Allow to cool slightly, filter, if necessary, on double Whatman No. 41 paper, add 10 ml of 1% potassium permanganate solution, stir until the solution has discolored and dilute to 250–300 ml with distilled water.

Electrolyze at a cathode potential of —0.15 V *vs.* S.C.E. which, during the electrolysis, should be altered gradually to —0.20 V *vs.* S.C.E. Electrolysis takes from 30 to

min. When it is complete, wash the calomel electrode, the cathode and the anode ith the washing solution; then wash the cathode with alcohol and ether, dry and igh.

Silver and bismuth which may be present, co-deposit with copper and must be termined separately. Some lead dioxide deposits at the anode during the electrolysis. The electrodes used were cylindrical, of the gauze type, with a height of 50 mm d a diameter of 35 mm (anode) or 53 mm (cathode); stirring was magnetic.

lloys analyzed and results obtained

The preparation of synthetic solutions of lead–base alloys by dissolving weighed nounts of the pure metals, according to the method, proved impossible: tin precipi- ted before all the copper was dissolved.

Therefore four synthetic alloys — 1000 g of each — were prepared by smelting refully weighed amounts of the pure metals in a graphite crucible heated in an ectric furnace. The lead was fused first and then the copper in wire form was added; n and the other metals were then added. The smelted alloy was protected by a layer

TABLE I
PERCENTAGE COMPOSITION OF THE ANALYZED ALLOYS

Alloy	Pb	Sn	Cu	Bi	Sb	Zn	Ni	Fe	Cd	As
1	70	27	1	—	1	1	—	—	—	—
2	55	41	1	—	1	2	—	—	—	—
3	71	24	0.5	0.5	1.5	0.4	0.1	2	—	—
4	68.95	28.75	0.3	—	1.5	0.1	0.1	0.1	0.1	0.1
5	bal.	8.85	0.26	tr.	4.18	tr.	—	tr.	tr.	tr.
6	40.99	44.00	4.91	—	10.13	—	—	—	—	—
177 A	bal.	4.64	0.33	0.03	12.04	0.08	—	0.06	—	0.06
53 C	bal.	5.16	0.214	0.093	10.20	—	0.0023	0.0017	—	0.044

graphite and then poured into small ingot moulds of steel; the surface layer was moved before the chips to be analyzed were shaved off.

Besides these synthetic alloys (designated as 1–2–3–4) two other alloys (Nos. 5 nd 6) already analyzed by the ASTM methods[4], as well as the standards No. 177 hite Metal A (British Chemical Standards) and No. 53 C (N.B.S.) were used in the sts. Table I shows the composition of these alloys.

The copper in alloys 1–2–3–4 was determined by the method proposed and tisfactory results (Table II) were obtained.

TABLE II

Alloy	1	2	3	4
	1.00	1.02	1.00	0.29
Cu %	0.99	1.03	1.02	0.32
(+ Bi %)	1.00	1.01	1.01	0.30
	0.99	1.03	1.01	0.30

In initial tests, perchloric acid and permanganate solution were not added but the st of the procedure was identical to that described above. Under these conditions,

copper took on a slightly dark appearance toward the end of the electrolysis, but th
results (Table III) were just as good.

TABLE III

Alloy	1	2	3	4
	0.99	1.01	1.02	0.32
Cu %	1.02	1.04	1.01	0.30
(+ Bi %)	1.01	1.02	1.03	0.31
	1.00	1.03	1.02	0.31

(2) *Antimony:* more than 1.5%.

When the alloy contained more than 1.5% of antimony and copper was determine
by the above method, after the almost complete deposition of copper (and bismuth
a co-deposition of antimony took place, whether perchloric acid was present or no

In such cases, near the end of electrolysis it was advisable to accelerate co-depo
sition by rendering the cathodic potential more negative, so that the current intensit
increased by 0.1–0.2 A. Electrolysis was stopped 5–10 min after the current ha
increased; in this way, it was certain that all the copper present had deposited.

In a tall-form 400-ml beaker, re-dissolve the deposit in 30 ml of dilute nitric aci
(1 + 3) containing 5 g of tartaric acid, heat to 70°–80° and, while still hot, add 1
of urea, dilute a little, add 3 g of succinic acid and 1 g of hydrazine dihydrochlorid
adjust the solution to pH 4.5–5 with ammonia, filter if traces of platinum are presen
owing to the reduction with hydrazine, and finally, electrolyze at —0.45 V vs. S.C.E.

By means of this double electrolysis satisfactory results (Table IV) were obtaine

TABLE IV

Alloy	5	6	177 A	53 C
Cu %	0.26	4.90	0.37	0.29
(+ Bi %)	0.26	4.93	0.37	0.30

(3) In presence of iron.

When 0.1 g of pure iron powder was added to the 5-g alloy sample and the solutio
was prepared for electrolysis by the above procedure without the addition of perchlor
acid and permanganate, the co-deposition of antimony — even if present in hig
percentage — was avoided. However, copper either did not deposit completely (
which case it retained its normal appearance) or the last particles that deposite
took on a dark color and then results were often high. In other words, the phenomer
were similar to those observed[9] when copper is electrolyzed in the presence of hig
percentages of iron.

Table V shows how satisfactory results and poor results alternated with a hig
percentage of antimony in the presence of iron. If perchloric acid was presen
antimony at high percentages co-deposited partially even when iron was presen
Because of this unstable behaviour, no advantage was obtained by adding iron
the alloy being analyzed.

TABLE V

Sample	Cu % in alloys							
	1	2	3	4	5	6	177 A	53 C
5 g of alloy + 0.1 g Fe	0.99	0.98	b	0.30	0.25	4.96	0.38	0.33
	0.99	1.00		0.29	0.26	5.07	0.34	0.29
	—	0.99		—	0.26	4.20	0.47	0.40
4 g of alloy + 0.5 g Sb + 0.1 g Fe^a	1.02	0.93	1.05	0.38				
	0.85	1.20	1.02	0.47				
	1.04	1.03	b	0.24				

he percentages refer to a 4-g sample.
1 g of Fe was not added to this alloy because it already contained 2% iron.

II. TIN–BASE ALLOYS

hod of analysis

n a 400-ml tall-form beaker weigh 5 g of alloy and add 50 ml of hydrochloric acid
– 1). Cover with a watch glass and heat moderately to dissolve almost all the
y: the residue left consists mainly of copper. At this point add, slowly and with
tion, some concentrated nitric acid: oxidation of tin and antimony takes place
irst, then copper starts dissolving. The reaction is rather violent and the beaker
uld be removed from the heating plate to prevent overflowing and excessive
ting that might precipitate tin.

nce the violent reaction ceases, all the alloy should be dissolved; if not, heat
derately and, if necessary, add a little concentrated nitric acid. Any slight opal-
nce caused by tin may be eliminated with a little concentrated hydrochloric acid.
e the alloy is completely dissolved, wash the watch-glass and the beaker walls
n a minimum of distilled water, heat slightly and add, little by little, up to 4–5 g
rea.

ext, add 10 g of tartaric acid, 2 g of succinic acid and 1 g of hydrazine dihydro-

TABLE VI

ANALYSIS OF TIN–BASE SYNTHETIC SOLUTION

All weights are in grams

Sn eighed	Sb Weighed	Cu				Pb			
		Weighed	%	Found	%	Weighed	%	Found	%
3459	0.3198	0.1049	2.10	0.1047	2.09	0.1595	3.19	0.1596	3.19
2973	0.3236	0.2640	5.28	0.2639	5.28	0.0257	0.51	0.0250	0.50
3808	0.3216	0.1165	2.33	0.1162	2.32	0.2053	4.11	0.2064	4.15
4185	0.3304	0.2066	4.15	0.2063	4.15	0.0104	0.21	0.0106	0.21
3956	0.3302	0.2627	5.25	0.2630	5.26	0.0232	0.46	0.0224	0.45
3365	0.3295	0.0994	1.99	0.0988	1.98	0.0468	0.94	0.0470	0.94
3286	0.3194	0.2566	5.15	0.2573	5.15	0.0342	0.68	0.0338	0.68
3798	0.3250	0.1125	2.25	0.1120	2.24	0.0560	1.12	0.0568	1.14
3495	0.3164	0.1512	3.02	0.1506	3.01	0.0148	0.29	0.0150	0.30
2381	0.3176	0.2023	4.05	0.2015	4.03	0.1045	2.09	0.1047	2.09
3327	0.3132	0.1958	3.92	0.1961	3.92	0.2428	4.86	0.2415	4.83
3503	0.3083	0.3038	6.08	0.3038	6.08	0.1034	2.07	0.1028	2.06
3226	0.3112	0.1345	2.69	0.1352	2.70	0.0534	1.07	0.0520	1.04
4574	0.3262	0.1381	2.65	0.1387	2.68	0.0395	0.79	0.0385	0.77
3291	0.3104	0.1651	3.30	0.1649	3.30	0.0137	0.27	0.0134	0.27

chloride. Adjust the solution to pH 4.8 to 5.2 with ammonia; narrow-range pH te
papers may be used, provided that the color of these papers at pH 4.8–5.2 has be
checked with a pH-meter. Deposit the copper at —0.30 to —0.40 V vs. S.C.E.; th
deposit lead on copper at —0.60 to —0.65 V vs. S.C.E. In both electrolyses, w
about 15 min after the current has dropped to a minimum constant value befc
washing and weighing the metals deposited on the cathode. Also in this case, silv
and bismuth co-deposit with copper.

Results from synthetic solutions

The preparation of tin–base alloy synthetic solutions from pure metals present:
no difficulty if lead was used as a very fine powder; otherwise the dissolution ti
was very long and tin precipitated.

Table VI shows the amounts of metals weighed and found, and the releva:
percentages of copper and lead referred to an assumed initial alloy sample of 5 g.

SUMMARY

In lead–base alloys, copper can be determined by a single controlled-potential electrolysis if l
than 1.5% of antimony is present; otherwise, the deposit must be dissolved and re-electrolyz
Iron tends to inhibit the co-deposition of antimony. In tin–base alloys, copper and lead can
determined successively. The sample weight is 5 g; percentages as low as 0.2% can be determin

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre dans des alliages à base de plomb, par élect
lyse à potentiel contrôlé. On a pu doser ainsi des teneurs en cuivre allant jusqu'à une lim
inférieure de 0.2%.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer in Bleilegierungen durch Elektrol
mit kontrolliertem Potential. Bei einer Einwage von 5 g können noch 0.2% Cu erfasst werd

REFERENCES

1 L. RAZSO, *Magyar Kém. Lapja*, 3 (1948) 37.
2 G. BUOGO AND L. RADOGNIA, *Ann. chim. appl.*, 38 (1948) 525.
3 P. FOERSTER, *Ann. chim. anal.*, 15 (1933) 441.
4 ASTM, *Methods of Chemical Analysis of Metals*, American Society for Testing Materials, Phil
  delphia 1946.
5 G. NORWITZ, *Anal. Chim. Acta*, 4 (1950) 539.
6 J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, New York 1953.
7 B. ALFONSI, *Anal. Chim. Acta*, 19 (1958) 276.
8 J. J. LINGANE AND S. L. JONES, *Anal. Chem.*, 23 (1951) 1798.
9 A. LASSIEUR, *Electroanalyse rapide*, Presses Universitaires, Paris 1927.

SEPARATIONS INVOLVING SULPHIDES

SEPARATION OF THORIUM OR TITANIUM FROM SOME ELEMENTS THAT FORM THIOSALTS

I. K. TAIMNI AND S. N. TANDON

Chemical Laboratories, University of Allahabad, Allahabad (India)

present investigation deals with the separation of thorium or titanium from
ments which can be estimated by decomposing their thiosalts with hydrochloric
d. The general method adopted was to treat the solution containing the two
als with sodium sulphide reagent and hydrochloric acid. The sulphide formed
then filtered and weighed, and thorium or titanium in the filtrate was determined
he oxinate or oxide respectively.

EXPERIMENTAL

ndard solutions of sodium arsenate, potassium antimony tartrate, potassium
urite, selenious acid, ammonium molybdate, mercuric chloride, gold chloride,
tinum chloride or potassium perrhenate and thorium sulphate or potassium titanyl
late were used.

*aration of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold,
tinum or rhenium from thorium*

asured volumes of the solutions were mixed and treated with 2 N sodium sulphide
gent in excess. A measured quantity of hydrochloric acid was added, the mixture
s heated to boiling and allowed to cool to room temperature. The precipitate was
ered on a sintered glass crucible (porosity 4), washed and weighed as As_2S_5[1],
$_2S_3$[2], TeS_2[1], SeS_2[1], $MoS_3 \cdot 2H_2O$[3], HgS[4], Au_2S_3[2], $PtS_2 \cdot 3H_2O$[5] or Re_2S_7[4]. The fol-
ving points should be noted:

. If a precipitate appears on mixing the two solutions, it need not be dissolved.
. For arsenic, platinum or rhenium the final acidity should be 6 N, for selenium 2
and for other elements 1 N.

he filtrate was then evaporated to about 50 ml to remove hydrogen sulphide,
ated to 250 ml and made barely acidic by addition of ammonium hydroxide. The
ution was heated to about 70°, 2% oxine solution in 2 N acetic acid was added
owed by 2 N ammonium hydroxide to precipitate the oxinate. The mixture
s allowed to cool to 50° and the precipitate was filtered on a sintered glass
cible, washed with water, dried between 100°–110° and weighed as $Th(C_9H_6ON)_4$,
$_7ON$[6].

30–38 mg of arsenic, 47–58 mg of antimony, 44–68 mg of tellurium, 33–60 mg
selenium, 32–40 mg of molybdenum, 68–85 mg of mercury, 9–23 mg of gold, 23–
mg of platinum or 37–46 mg of rhenium were separated from 32–40 mg of thoriur

The metals were recovered with an accuracy of:

As, —0.5% to + 0.25%; Sb, —0.19% to 0.0%; Te, 0.0%; Se, —0.37% to 0.0%
Mo, 0.0% to + 1.0%; Hg, —0.2% to + 0.25%; Au, 0.0%; Pt, —0.43% to + 0.27%
Re, —0.54% to 0.0%; Th, 0.0% to + 0.45%; Th, —0.15% to + 0.12%; Th, 0.0%
+ 0.97%; Th, —0.24% to 0.0%; Th, —0.12% to + 0.97%; Th, 0.0% to + 0.45%
Th, —0.75% to + 0.36%; Th, —0.6% to + 0.48%; Th, ± 0.75%.

Separation of antimony, tellurium, selenium or mercury from titanium

Antimony, tellurium, selenium or mercury were determined as above as Sb_2S_3
TeS_2[1], SeS_2[1] or HgS[4] respectively. In the filtrate titanium was determined by precip
tation with cupferron and ignition to TiO_2[7].

47–58 mg of antimony, 54–68 mg of tellurium, 33–41 mg of selenium, 68–85 m
of mercury were separated from 39–49 mg of titanium. The metals were recovere
with an accuracy of:

Sb, 0.0% + 0.24%; Te, —0.19% to 0.0%; Se, 0.0%; Hg, —0.25% to 0.0%; T
—0.3% to 0.0%; Ti, —0.3% to 0.0%; Ti, 0.0% to + 0.6%; Ti, —0.24% to + 0.3%

SUMMARY

Sodium sulphide can be used to separate arsenic, antimony, tellurium, selenium, molybdenur
mercury, gold, platinum or rhenium from thorium and antimony, tellurium, selenium or mercur
from titanium.

RÉSUMÉ

Le sulfure de sodium a été utilisé pour la séparation de l'arsenic, de l'antimoine, du tellure,
sélénium, du molybdène, du mercure, de l'or, du platine ou du rhénium d'avec le thorium
également pour séparation de l'antimoine, du tellure, du sélénium ou du mercure d'avec le titan

ZUSAMMENFASSUNG

Die Trennung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin od
Rhenium von Thorium und die von Antimon, Tellur, Selen oder Quecksilber von Titan kann m
2 N Natriumsulfid erzielt werden.

REFERENCES

[1] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 121.
[2] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 10 (1954) 312.
[3] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 203.
[4] I. K. TAIMNI AND G. B. S. SALARIA, *Anal. Chim. Acta*, 12 (1955) 519.
[5] G. B. S. SALARIA, *Anal. Chim. Acta*, 17 (1957) 395.
[6] T. MOELLER, G. K. SCHWEITZER AND D. D. STARR, *Chem. Revs.*, 42 (1948) 91.
[7] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMANN, *Applied Inorgan
Analysis*, John Wiley and Sons, New York 1953, p. 585.

DIRECT DETERMINATION OF TRACES OF TOTAL OXYGEN IN NAPHTHAS

I. J. OITA

Research and Development Department, Standard Oil Company, Whiting, Ind. (U.S.A.)

aces of oxygen in elementary and combined form in naphtha have become impor-
at in various petroleum-refining processes. Dissolved elemental oxygen causes
ling in heat exchangers[1]. Traces of water impair the activity of reformer cata-
ts[2]. Sometimes the undesirable constituent is carbon dioxide, carbon monoxide,
some other oxygenated compound. Although specific methods for each type of
ygen compound are available, there has been no satisfactory method of directly
ermining the total oxygen content of low-boiling petroleum distillates.

The direct determination of total oxygen in organic substances has been the
ject of many recent papers[3-11]. Methods most widely used have been modifica-
ns of the SCHÜTZE method[9], in which the sample is pyrolyzed over carbon at about
00°. The oxygen is quantitatively converted to carbon monoxide and, after oxida-
n to carbon dioxide, is determined manometrically[6], volumetrically[5], gravimetri-
lly[4,8,9], or iodometrically[3,11]. However, these modifications are not accurate
low 0.1% oxygen.

Nevertheless, the SCHÜTZE method could be used for determining trace amounts
oxygen in light hydrocarbons if the problems of sensitivity and volatility were
ercome. To obtain a measurable amount of carbon dioxide, a large sample must
pyrolyzed. To prevent dangerous explosions, the pyrolysis rate must be carefully
gulated. To minimize evaporation, during weighing and handling the sample must
enclosed in a container having relatively small openings. Provision must be made
purge atmospheric oxygen from the system after the sample is placed inside the
rolysis tube. Finally, the sample container must remain inert at the pyrolysis
mperature.

Fulfillment of these strict requirements was made possible by handling the sample
the magnetically controlled spiral shown in Fig. 1[7], rather than in a boat. Made of
artz, it is open at both ends and has a small quartz hook at one end. Evaporation
ring weighing and purging is minimized by the small open ends. The spiral can be
mpletely filled without entrapping any air.

The spiral is manipulated by a bar magnet completely enclosed in quartz, with a
ok on one end to engage the hook on the spiral. Spiral and manipulator can be
ntrolled as a unit from the outside of the pyrolysis tube by an external magnet.
otating the external magnet about the pyrolysis tube in the region of the manipula-

tor rotates both it and the spiral. With each rotation, a small amount of sample
expelled from the end of the spiral.

With this sample-handling device, a satisfactory method has been developed f
the trace determination of oxygen in naphtha. A modification[8] of the SCHÜT
method was used as the basic procedure, although some changes were made in bo
the apparatus and operating procedure. In the apparatus: (a) a longer and larg
pyrolysis tube was used to accommodate the spiral; (b) a larger furnace was necessa
to give a longer heating zone; (c) a longer platinized-carbon filling was used to i
crease the life of the filling; (d) large granules of carbon were placed at the front
the platinized-carbon filling to smooth the flow of nitrogen; and (e) a removable rc
of platinum gauze was placed in front of the carbon filling to collect pyrolytic carbo
In the operating procedure, the reverse purge was extended and appropriate chang
were made to accommodate the use of the spiral.
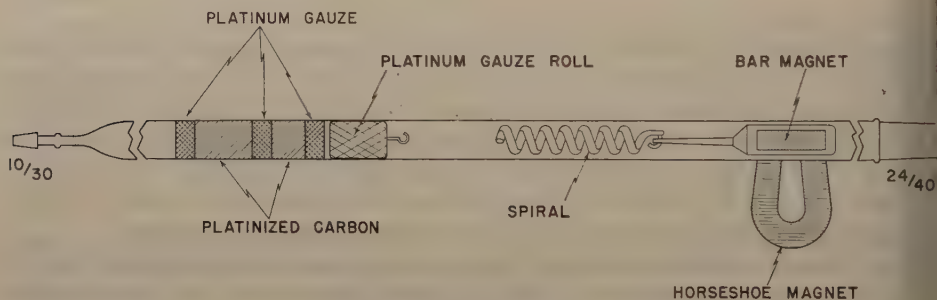
Fig. 1. Pyrolysis tube.

EXPERIMENTAL

Apparatus

Except for the pyrolysis tube, shown in Fig. 1, the rest of the train is as described previously
The clear quartz pyrolysis tube is 20 mm in outside diameter and 70 cm long, with a Pyrex-t
quartz graded seal at each end.

The spiral is about 15 mm in diameter and made from 5 to 20 turns of quartz tubing 5 to 7 m
in outside diameter. As determined by the diameter and number of turns, the capacity rang
from 0.5 to 5 g of sample. Spirals of several sizes should be available.

The manipulator contains a bar magnet about 6 mm in diameter and 25 mm long. A horsesh
magnet is used as the external magnet.

The carbon filling is 10 cm long, retained at the ends and divided into two portions by 1-c
lengths of platinum gauze. A roll of platinum gauze 3 cm long is placed just before the fro
endplug to minimize deposition of pyrolytic carbon on the platinized carbon. The roll should
loose enough that it can be pulled out of the tube periodically to burn off the carbon.

Procedure

Sweep the apparatus with nitrogen for two hours at room temperature and then turn on a
furnaces. Adjust the flow rate to 10 ml per min. After the pyrolysis-tube furnace is at 900
continue purging the apparatus for at least four hours.

Weigh a spiral of appropriate size and fill it by connecting it to a small syringe and vertical
drawing up the sample through the open end. There must be no enclosed air in the spiral. Weig
the sample to the nearest milligram.

Reverse the nitrogen flow and increase it to 30 ml per minute. Insert the spiral and the manip
lator in the tube. Position the two units so that the spiral is about 4 inches from the furnac
Close the inlet joint and continue the reverse purge. To minimize volatilization of the samp
place a Dry Ice pack around the section of the pyrolysis tube containing the spiral. After 10 m
of reverse purge, change to a forward flow, reduce it to 10 ml per min, and remove the Dry I
pack. During the reverse purge, weigh the microabsorber on a microbalance.

ring the spiral to about 1 inch from the furnace. Rotate the spiral and expell a small amount of
ble. If the deposited sample does not volatilize, move the spiral slightly closer to the furnace.
iinue expelling small increments of sample as rapidly as possible without causing the entering
of nitrogen through the flowmeter to fall below 2 ml per min. When rotation no longer expels
sample, carefully heat the pyrolysis tube with a low flame of a Bunsen burner, starting from
int 3 inches further from the furnace than the manipulator, and slowly moving the burner up
he furnace. Repeat the heating with a maximum flame.
ter 40 min of sweeping with nitrogen, remove and weigh the micro-absorption tube.
un a blank with an empty spiral which has been flushed with nitrogen. Utilize a reverse-purge
5 min, and weigh the microabsorption during this period. Return the absorber to the train,
ge to a forward flow, and heat the tube with the maximum flame of a Bunsen burner. Sweep
o min and reweigh the microabsorption tube.
ulate the per cent oxygen by the equation:

$$\% \text{ oxygen} = \frac{36.36(W_1 - W_2)}{W_3}$$

re W_1 is the weight of CO_2 from the sample, W_2 is the weight of CO_2 from the blank, and W_3
e weight of sample.
fter every 8 to 10 runs, the removable roll of platinum gauze should be taken out and the
olytic carbon should be burned off with a Bunsen burner. At this time, the carbon accumulated
he inside of the pyrolysis tube can be burned off by inserting a small quartz tube through the
ple-inlet joint and introducing air against a reverse flow of nitrogen while the pyrolysis tube
eated with a Bunsen burner. To avoid high results after this burn-off, the pyrolysis tube can
econditioned by passing hydrogen through it at 700° for 10 min. Hydrogen treatment is also
ful in conditioning fresh platinized carbon. Hydrogen is an excellent desorption gas and
oves the adsorbed oxygen on the pyrolysis tube.

RESULTS AND DISCUSSION

test the over-all efficiency of the train, highly oxygenated nonvolatile com-
nds were analyzed. To test the accuracy and precision of the method for trace
ermination of oxygen in naphtha, solutions containing known amounts of cetyl
hol in iso-octane were prepared and analyzed. These test samples were inter-
rsed with a wide variety of routine samples.
Analyses of highly oxygenated nonvolatile samples are shown in Table I. Because
y were solid samples, a platinum boat was used in place of the spiral. The results
ained with these samples show that all of the oxygen is being converted to carbon
noxide and subsequently oxidized to carbon dioxide by the iodine pentoxide.

TABLE I

ANALYSES OF OXYGENATED COMPOUNDS

(Oxygen, weight %)

Sample	Theory	Found ($\overline{X} + s$) [a]
Cetyl alcohol	6.60	6.61 ± 0.10
Acetanilide	11.84	11.82 ± 0.14
Benzoic acid	26.20	25.97 ± 0.13

[a] Average of 3 determinations.

od results were obtained even with benzoic acid, which is difficult to pyrolyze to
rbon monoxide.
Analyses of synthetic samples prepared by adding known amounts of cetyl alcohol
iso-octane are shown in Table II. The iso-octane was purified by percolation
rough a 24-inch column of 8 to 200 mesh adsorption alumina. Aside from keeping
samples under a nitrogen blanket in the container and exercising the usual care

TABLE II

ANALYSES OF SOLUTIONS OF CETYL ALCOHOL IN ISO-OCTANE

(Oxygen, p.p.m.)

Calculated	Found				Mean	Standard deviation	Average error
125	149	129	126		135	9	10
144	169	142	159		157	14	14
202	173	219	236	209	209	26	22

in oxygen analysis, no special effort was made to exclude atmospheric oxygen water vapor. In order to exclude completely atmospheric oxygen or water vapor, very elaborate system of sampling, weighing, and sample insertion would be require Even if such a system were used, the accuracy of the method may not be improv as the sample would be subjected to the oxygen-free atmosphere of such a syste and might lose some dissolved oxygen or water vapor.

Air-saturated naphtha generally contains 30 to 80 p.p.m. of dissolved oxygen the calculated values for the synthetic samples include the average value of 51 p.p.r oxygen found in the iso-octane. Standard deviations range from 9 to 26 p.p.r oxygen, and the average error is about 10% cent of the oxygen present. Reasons f the positive error are not known.

TABLE III

ANALYSES OF LIGHT HYDROCARBONS

(Oxygen, p.p.m.)

Light naphtha A		43	65
Light naphtha B		83	112
Light naphtha C		123	134
Hydrodesulfurized naphtha D		14	30
Hydrodesulfurized naphtha E		23	34
Iso-octane, purified	44	53	57
Iso-octane, knock-testing grade			530
Alphamethylnaphthalene			648

Analyses of typical naphtha samples are shown in Table III. The values obtain for the light naphthas are typical of reformer feeds, which usually contain 20 to p.p.m. of water. The deviations for duplicate values are about ± 20% from the mea The hydrodesulfurized naphthas were run as soon as possible after they were take from refinery units. The knock-testing iso-octane was purified by percolation throug alumina and used to prepare the cetyl alcohol solutions in Table II.

Blank values range from 0.02 to 0.05 mg of oxygen (somewhat higher than th 0.007 mg reported earlier[8]). The high blank is probably due to the larger samp container and the larger pyrolysis tube, which offer more surface area for adsorbir air. However, with the 10 to 20-fold increase in sample size, precision remains hig

As an extension of the method, an attempt was made to determine trace oxyg in liquefied gases, such as butene. The sample was introduced from a glass bor having a metal needle valve, which was connected to the stopcock near the sampl

joint. About 2 g of sample were bled into the system in one hour, and the oxygen determination was carried out in the usual way. Values of 680 and 86 p.p.m. total oxygen were obtained on two butene samples. Karl Fisher water values on the same samples were 520 and 40 p.p.m. oxygen, respectively. After six satisfactory runs, exceedingly high values were obtained. Apparently the butene was passing through the platinized carbon and being oxidized to carbon dioxide by the iodine pentoxide. Pyrolytic carbon was not formed on the platinum gauze but deposited on the platinized carbon itself, such that it became unreactive after six determinations. Thus, although the method is reliable for butene-type samples, frequent refilling of the pyrolysis tube is necessary if many are to be run.

SUMMARY

The low oxygen content and volatility of naphthas make existing methods for determining traces of oxygen and oxygen compounds in naphthas unreliable. The SCHÜTZE method has been modified to include a magnetically controlled spiral sample container from which a 5-g sample can be pyrolyzed safely by expelling it a few drops at a time. In the range of 100 to 200 p.p.m. oxygen, the standard deviation and the average error for synthetic samples are about 10% of the oxygen present. The deviation from the mean for routine samples containing less than 100 p.p.m. oxygen is about ± 20%.

RÉSUMÉ

L'auteur propose une modification de la méthode de SCHÜTZE, permettant le dosage de faibles quantités d'oxygène (combiné et libre) dans des fractions d'huiles minérales facilement volatiles.

ZUSAMMENFASSUNG

Es wird eine modifizierte Methode der Sauerstoffbestimmung nach SCHÜTZE beschrieben, die erlaubt, Spuren von Sauerstoff (frei oder gebunden) in leicht flüchtigen Erdölfraktionen zu bestimmen.

REFERENCES

J. A. BIEHL AND W. T. MADDOCK, *Petrol. Processing*, 11 (1956) 98.
W. P. HETTINGER, C. D. KEITH, J. L. GRING AND J. W. TETER, *Ind. Eng. Chem.*, 47 (1955) 719.
R. A. DINERSTEIN AND R. W. KLIPP, *Anal Chem.*, 21 (1949) 545.
M. DUNDY AND E. STEHR, *Anal. Chem.*, 23 (1951) 1408.
R. D. HINKEL AND R. RAYMOND, *Anal. Chem.*, 25 (1953) 470.
J. HOLOWCHAK AND G. E. C. WEAR, *Anal. Chem.*, 23 (1951) 1404.
I. J. OITA, *U. S. Patent No. 2, 774, 588*, December 1956.
I. J. OITA AND H. S. CONWAY, *Anal. Chem.*, 26 (1954) 600.
M. SCHÜTZE, *Z. anal. Chem.*, 118 (1939) 241.
I. SHEFT AND J. J. KATZ, *Anal. Chem.*, 29 (1957) 1322.
J. UNTERZAUCHER, *Analyst*, 77 (1952) 584.

A DINITROPHENYLATION METHOD FOR THE MICRO-DETERMINATION OF AMIDE NITROGEN

J. H. BRADBURY

Division of Textile Industry, Wool Research Laboratories, C.S.I.R.O. Geelong (Australia)

(Received October 12th, 1959)

INTRODUCTION

Amino acid analysis of cuticle-rich material from three samples of wool has sho[wn] that the cuticle is consistently poor in glutamic acid plus glutamine and aspa[rtic] acid plus asparagine[1]. It is therefore important to determine the amide-nitrog[en] content of both cuticle and whole fibre so that the amount of glutamic and aspa[rtic] acid present can be calculated. It seemed that this might be possible on a microsc[ale] by making use of the unwanted spot of 2,4-dinitroaniline ($DNPNH_2$), produced [by] reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and ammonia which is alwa[ys] present on the two dimensional paper chromatogram of the dinitrophenyl-am[ino] acids. The problem of quantitative evolution of ammonia from the wool protein [by] hydrolysis in hydrochloric acid had been thoroughly investigated by LEACH A[ND] PARKHILL[2]. However, LOCKHART[3] found only 50% reaction of FDNB with ammo[nia] as compared with its quantitative reaction with a number of amines and this [is] paralleled by kinetic evidence on the reaction between 1-chloro-2,4-dinitrobenze[ne] and these compounds[4].

This paper describes a satisfactory method for the analysis of amide-nitrogen [in] 0.5-mg samples of cuticle-rich material from wool.

EXPERIMENTAL AND RESULTS

Materials

Samples of Lincoln 36's and Corriedale 46's greasy wool were separated into base and tip [and] the grease removed as described previously[5]. A third sample of Lincoln 36's wool processe[d in] top form was likewise cleaned and all samples conditioned at 65% R.H. and 20°. The 2 N HCl [for] hydrolysis was prepared by dilution of twice-distilled 6 N HCl with glass distilled water b[efore] freshly distilled. Acetone (A.R.) was refluxed with $KMnO_4$ and then fractionated to remove [the] traces of alcohols[6]. A sample of FDNB (British Drug Houses Ltd., Poole, Dorset) was fractio[nally] distilled at 0.5–1.0 mm Hg-pressure at 116° to produce a light yellow product which was sto[red] at 2°. Peroxide free diethyl ether (A.R.) was freed from quinones before use by extraction w[ith] 1% aq. NaOH (four times), dilute HCl (once) and distilled water (four times). Laboratory gr[ade] $DNPNH_2$ was not recrystallised since it was found to be chromatographically pure. Ammon[ium] chloride, $KHCO_3$ and glycine were A.R. reagents used without further purification.

Preliminary experiments

The reaction between NH_3 and FDNB in aqueous solution at 40° by the met[hod] of LEVY[7], produced only 25% of $DNPNH_2$ even after 7 h heating. Reaction i[n a] homogeneous solution of ethanol and 0.5 M $KHCO_3$ solution (2:1) according [to]

GER[8] gave much higher yields of $DNPNH_2$ but produced large quantities of
[e]yl 2,4-dinitrophenyl ether[4]. This compound, together with the $DNPNH_2$, was
[extr]acted by ether from the aqueous solution after dinitrophenylation and on a one-
[dim]ensional paper chromatogram ran just faster than $DNPNH_2$, but overlapped
[wit]h it in a large range of solvents. It gave a colorless spot which showed up under
[U.V]. light and gave a strong absorption at 345 mμ, the absorption maximum for
[DN]PNH$_2$ in N HCl. To eliminate the interference of this material the reaction was
[rep]eated, ethanol being replaced by methanol, dioxan and acetone. With methanol,
[me]thyl 2,4-dinitrophenyl ether was produced which interfered in the chromatog-
[rap]hy, dioxan gave low yields but acetone appeared to be a satisfactory solvent.
[In] order to increase the rate of reaction between NH_3 and FDNB the temperature
[of r]eaction was raised to 50° and a series of experiments carried out according to the
[foll]owing procedure.

[A]n aqueous solution containing exactly 0.020 mg of A.R. NH_4Cl was evaporated
[to]dryness, 1.0 ml 0.5 M KHCO$_3$ solution added by an automatic pipette followed by
[2]ml acetone containing FDNB. After heating at 50° in a small stoppered flask for
[an] appropriate time, 1 ml of a 5% solution of glycine was added and the heating
[con]tinued for a further 30 min in order to remove all excess FDNB[3]. Five ml 0.5 M
[KH]CO$_3$ was added, the solution extracted with ether (5 × 5 ml) and the combined
[eth]er extracts divided accurately into two parts. These were evaporated to dryness,
[the] yellow residues dissolved in the minimum of acetone and applied as spots to
[Wh]atman No. 1 paper buffered with 0.1 M phthalate buffer at pH 5. The chromato-
[gra]ms were run in one dimension using 2-methylbutan-2-ol saturated with pH 5
[ph]thalate buffer[9] for 16 h, and the spot due to $DNPNH_2$ identified by comparison
[wit]h the pure $DNPNH_2$ run on the same paper. The paper was dried, the $DNPNH_2$
[spo]t excised and its weight, together with that of three paper blanks, determined.
[Th]e yellow colour was eluted with 5 ml N HCl at room temperature for 30 min and
[me]asured at its absorption maximum (345 mμ) in a 1-cm matched cell of the Unicam
[spe]ctrophotometer. The small blank correction, about 0.01/100 mg of paper, was
[sub]tracted from the observed optical density. A further correction, amounting to
[20]–30% of the total observed optical density, was made for the amount of ammonia
[pr]esent in the reagents used. This correction varied in amount from one series of
[ex]periments to the next and was estimated by running one control experiment with
[eac]h series. From the corrected value of the optical density the % yield of $DNPNH_2$
[ob]tained from the NH_4Cl was calculated using the experimentally obtained value

TABLE I

YIELD OF $DNPNH_2$ FROM AMMONIA BY DINITROPHENYLATION

Weight FDNB mg	Time of heating min	% Yield (mean of < 2 determinations)
5	180	65
10	180	72
20	180	82
30	180	78
20	20	69
20	45	80
20	90	72

of the molar extinction coefficient for pure DNPNH₂ in N HCl of $(1.43 \pm 0.027) \cdot 1$

The results in Table I show the effect of variation of the amount of FDNB a time of heating on the yield of DNPNH₂. It is clear that about 20 mg of FDNB required to give about 80% yield but there is no improvement on increasing t amount to 30 mg. Similarly 45 min reaction time gives about 80% yield but there no advantage in increasing the time to 180 min. It therefore appears that the maximu yield obtainable is about 80% and it is interesting that the 20% loss of ammon and/or DNPNH₂ during reaction and chromatography agrees very closely with t losses previously found in the dinitrophenylation of the amino acids[10]. In order estimate possible losses of DNPNH₂ by further substitution of the primary amin group by dinitrophenyl groups and by extraction and chromatography, micr amounts of DNPNH₂ were carried through the above procedure and the % recover of DNPNH₂ on the chromatogram estimated. This amounted to 91.5% showing th there is a loss of 8.5% of DNPNH₂ in this way. It is unlikely that the additional lo of 11.5% of material is due to incomplete reaction between ammonia and FDN since more stringent conditions of reaction do not increase the yield. It is possib that some ammonia could react with acetone[11] but this would still not explain th very similar results obtained in the dinitrophenylation of the amino acids[10].

For practical purposes the yield is constant at 80%, giving $\varepsilon = (1.14 \pm .036) \cdot 1$ as the mean of 10 experiments (excluding rows 1, 2 and 5 of Table I). This figure used in all future experiments together with 20 mg FDNB and a heating period 1 h at 50°.

Final procedure

A sample of cuticle-rich material, obtained as described previously[1] or whole fibr weighing about 0.5 mg was placed in a clean test tube, 3 ml 2 N HCl added and th tube closed with a spring-loaded ground glass stopper. The tube was heated at 10 for 2 h[2], after which time only a slight residue remained. An alternative techniqu of sealing the tube under vacuum and heating at 105° in the oven gave irreproducibl results. The hydrochloric acid was evaporated at the water pump, 1.0 ml 0.5 M KHCO₃ added by an automatic pipette followed by a solution of 20 mg FDNB i 1.5 ml acetone. After heating at 50° for 1 h, 1 ml of 5% aqueous glycine was adde and the heating continued for 30 min. Five ml 0.5 M KHCO₃ was added and th DNPNH₂ extracted from the aqueous solution with ether (5 × 5 ml). The ethe extract was divided into two equal parts by volume, the ether evaporated at th

TABLE II

Amide nitrogen content of whole fibre and cuticle-rich material (moles/10^4 g material at 65% R.H and 20°) with standard errors

Sample of wool	Amide-N content of		Mean % cuticle material removed from the fibre
	whole fibre	cuticle-rich material	
Lincoln 36's, virgin wool, tips removed	7.0 ± 0.2	7.2 ± 0.5	0.69
Lincoln 36's, processed to top form	7.4 ± 0.4	7.4 ± 0.6	0.56
Corriedale 46's, virgin wool, tips removed	7.3 ± 0.2	6.1 ± 0.1	0.50

mp and the yellow residue chromatographed as described above. The spots due
DNPNH₂ were excised, eluted with 5 ml N HCl for 30 min at room temperature
l the optical density measured at 345 mμ. After correction was made for the paper
nk and the amount of ammonia in the reagents as described above, the optical
sity was used to calculate the amide-N content of the protein material in moles/
g material at 65% R.H. and 20°, using the value of the molar extinction coefficient
1.14 · 10⁴.

he figures for the amide nitrogen content of whole fibre and cuticle material
orded in Table II represent the means of at least four analyses.

n order to check whether the abrasive action of the descaler had any effect on
amide-nitrogen value the sample of Lincoln 36's virgin wool was rubbed back
l forth across a very sharp abrasive edge until breakage occurred. Four analyses
which an average of 5.7% of material was abraded from the fibre gave a mean
ue of 7.6 ± 0.4 moles/10⁴ g material at 65% R.H. and 20°. This is not significantly
fferent from the whole fibre figure of 7.0 ± 0.2 hence showing that abrasion does
alter the amide-nitrogen content of the material.

DISCUSSION

om the results in Table II it is clear that the amide content of the cuticle-rich
terial is the same as that of the whole fibre for both samples of Lincoln 36's wool.
owever, this is not the case for the Corriedale 46's sample where the cuticle-rich
terial is significantly poorer in amide groups than the whole fibre. Differences in
haviour from one sample of wool to the next must therefore be expected. The more
portant use of these figures is in the calculation of the aspartic acid and glutamic
id content of the cuticle-rich material[12].

The results obtained for whole fibre analyses agree well with the value of 7.1
oles/10⁴ g wool at 65% R.H. and 20° calculated from the results of LEACH AND
RKHILL[2] on Lincoln 36's wool. The mean standard error calculated over all sets
results is 4.5%. This figure is quite reasonable for such a determination which
volves the use of extraction and paper chromatographic techniques and is to be
mpared with an overall mean standard error for amino acid determination of
)%[12]. The minimum amount of ammonia which can be estimated accurately by
is method is about 2 μg. However if the amount of ammonia in the reagents could
reduced it should be possible to determine as little as 0.5 μg ammonia (40 μg wool)
ite accurately.

SUMMARY

new micro-method is reported for the determination of amide nitrogen, based on the estima-
on of 2,4-dinitroaniline produced by the reaction between ammonia, quantitatively liberated
om the protein, and 1-fluoro-2,4-dinitrobenzene. Application of the method to 0.5-mg samples
wool gives results in agreement with those obtained by other authors for the same type of wool.
nalyses of cuticle-rich material obtained from these wool samples show that in one sample out
three the cuticle is significantly poorer in amide groups than the whole fibre. The mean standard
ror taken over all the analyses is 4.5%.

RÉSUMÉ

Une nouvelle méthode microchimique est proposée pour le dosage de l'azote des amides. E
est basée sur une détermination de la dinitro-2,4-aniline, produite par la réaction entre l'amm
niac, quantitativement libéré de la protéine et le fluoro-1-dinitro-2,4-benzène.

ZUSAMMENFASSUNG

Es wird eine neue mikrochemische Methode beschrieben zur Bestimmung von Amid-Stickstc
Das aus dem Protein in Freiheit gesetzte Ammoniak wird mit Fluoro-1-dinitro-2,4-benzol
Reaktion gebracht und das entstandene Dinitro-2,4-anilin bestimmt.

REFERENCES

1 J. H. BRADBURY, Nature, 183 (1959) 305.
2 S. J. LEACH AND M. J. PARKHILL, Proc. Intern. Wool Textile Research Conf., Melbourne 19
    Vol. C., p. 92.
3 I. M. LOCKHART, Nature, 177 (1956) 393.
4 J. F. BUNNETT AND R. E. ZAHLER, Chem. Revs, 49 (1951) 273.
5 J. H. BRADBURY, Biochem. J., 68 (1958) 482.
6 A. WEISSBERGER, E. S. PROSKAUER, J. A. RIDDICK AND E. E. TOOPS, Organic Solvents, 2nd E
    Interscience Publishers Inc., New York 1955, p. 379.
7 A. L. LEVY, Nature, 174 (1954) 126.
8 F. SANGER, Biochem. J., 39 (1945) 507.
9 H. FRAENKEL-CONRAT, J. I. HARRIS AND A. L. LEVY, Methods of Biochemical Analy
    Vol. 2, Ed. by D. GLICK. Interscience Publishers Inc., New York 1955, p. 360.
10 J. H. BRADBURY, Biochem. J., 68 (1958) 475.
11 R. B. BRADBURY, N. C. HANCOX AND H. H. HATT, J. Chem. Soc., (1947) 1394.
12 J. H. BRADBURY, Textile Research J., in the press.

A SIMPLE SPECIFIC TEST FOR INNER-RING *o*-QUINONES

E. SAWICKI AND W. ELBERT

*Air Pollution Engineering Research, Robert A. Taft Sanitary Engineering Center, U.S. Departm
of Health Education and Welfare, Public Health Service, Cincinnati, Ohio (U.S.A.)*

INTRODUCTION

In a previous paper[1] a thermochromic test for the detection of inner-ring *p*-quino
and fluorenones was described. This test gave positive results with the aroma
fraction of airborne particulates. With a modification of the procedure[2], ber
fluorenes were detected in the air for the first time[3]. In another modified form the
has also been used to confirm the presence of anthracene in the air[3]. A test for termin
ring *o*- and *p*-quinones has also been described recently[4]. Since a specific method
the detection of inner-ring *o*-quinones is not available in the literature, such a met
has been developed.

The test procedure is based on the reported preparation of the bis-anils of chrys
quinone[5].

The following reaction probably contributes to some extent to the overall mecha-
[ni]sm of color formation:

Yellow   Blue
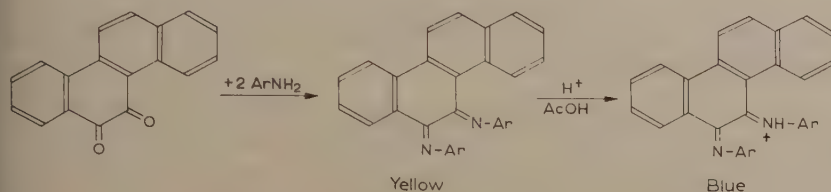
[in]line with this mechanism is the reversible decolorization of the blue color by alkali
[and] the report by SINGH AND DUTT[5] that the brown bis-(o-methoxyanil) of 5,6-
[chr]ysenequinone has a wavelength maximum at 587 mμ (probably in acetic acid).

EXPERIMENTAL

[Re]agents and equipment

[3],4-Dimethoxyaniline and 9,10-phenanthraquinone were obtained from the Aldrich Chemical
[Co.], Milwaukee 12, Wisconsin. Dibenz[a,h]anthra-5,6-quinone was donated by Dr. VINCENT
[DE]VERIO. 5,6-Chrysene-quinone[5] and 9,10-retenequinone[6] were prepared by the oxidation of
[chr]ysene and retene, respectively.
[A] Cary Model 11 Recording Spectrophotometer was used for wavelength measurements.

[Spo]t test procedure

[To] one drop of an acetic acid test solution in a 5-ml centrifuge tube add one
[dr]op of a 1.4% solution of 3,4-dimethoxyaniline in acetic acid. The mixture was
[he]ated on a water bath for 20 min. A blue to green color was formed in the presence of
[an] inner-ring o-quinone.

[C]olorimetric procedure

[To] one ml of an acetic acid test solution in a 10-ml volumetric flask was added 1 ml
[of] the reagent (1.4% 3,4-dimethoxyaniline in acetic acid). The mixture was heated
[on] a water bath for 20 min, cooled and then diluted to the mark with acetic acid.
[A] blank was run concurrently. The presence of inner-ring o-quinones was shown by
[th]e presence of a blue color and a wavelength maximum near 600 mμ. The results
[fro]m the spot test and colorimetric procedures are shown in Table I.

TABLE I

3,4-DIMETHOXYANILINE TEST FOR INNER-RING o-QUINONES

Compound	Colorimetric test[a]		Spot test identification limit, μg
	λ_{max}	$\varepsilon \cdot 10^{-3}$	
9,10-Phenanthraquinone	590	16.5	12
9,10-Retenequinone	615	12.3	15
5,6-Chrysenequinone	615	12.3	5
Dibenz[a,h]anthra-5,6-quinone	590	17.1	18

[a] ε = molar extinction coefficient (concn. in gmoles/l).

DISCUSSION

Many aromatic amines were tried as the reagent in the test, but 3,4-dimethoxyanili
appears to be the best. A brilliant blue color was obtained with all the o-quinones
the colorimetric procedure (Table I). The identification limits in the spot test proc
dure ranged from 5 to 18 μg.
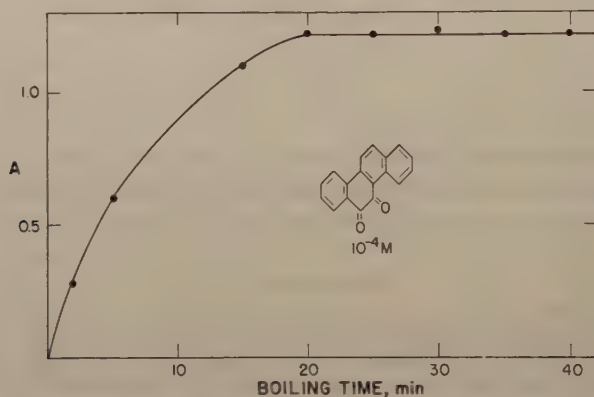
Fig. 1. Effect of time of boiling on absorbance at λ_{max} 615 mμ. Reaction of 5,6-chrysenequino
with 3,4-dimethoxyaniline by the standard colorimetric procedure.

The colorimetric procedure for 5,6-chrysenequinone was fully investigated. T
reaction mixture had to be heated for at least 20 min at 100° for maximum col
development (Fig. 1). The color was stable for at least 14 h. The volume of reage
was not critical. However, at least 1 ml was necessary for maximum color develo
ment (Fig. 2).

The following compounds gave negative results in the spot test procedure: benz
chloranil, 1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 4-sulfo-1,2-nap
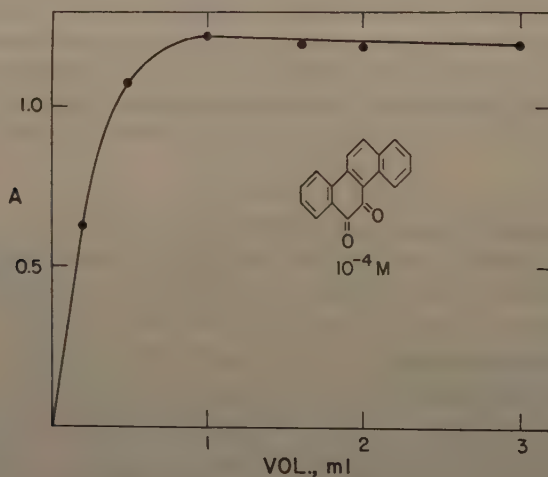
Fig. 2. Effect of volume of reagent (1.4% 3,4-dimethoxyaniline in acetic acid) on absorbance
615 mμ. Reaction of 5,6-chrysenequinone with reagent by standard procedure.

quinone, fluorenone, acenaphthenequinone, anthraquinone and benzanthrone.
1,4-naphthoquinones gave a scarlet color.

The presence of oxidants such as chromic acid could interfere in the color test, since a blue color, λ_{max} 585 mμ, is obtained immediately and without heat upon reaction of the oxidant with the reagent in the acetic acid. However, quinones should be easily separated from such an oxidant.

Another characteristic of the inner-ring o-quinones was the blue to green color they gave in sulfuric acid (Table II). The wavelength maxima of these solutions ranged from 585–670 mμ. The long wavelength band of the phenanthraquinones was approximately one-tenth the intensity of the analogous band of the other quinones.

TABLE II

COLORS, WAVELENGTH MAXIMA, MOLAR ABSORBANCES AND IDENTIFICATION LIMITS OF o-QUINONES IN SULFURIC ACID

| Compound	Color	λ_{max}, mμ	$\varepsilon \cdot 10^{-3}$	Identification limit, μg
o-Phenanthraquinone	green	630	1.2	40
o-Retenequinone	green	670	1.7	16
Chrysenequinone	blue	585	12.5	3
benz[a,h]anthra-5,6-quinone	green	655	10.5	5

Although this characteristic could prove of value in the characterization of the quinones, it must be emphasized that other types of compounds — quinonic and non-quinonic — give a blue to green color in sulfuric acid.

SUMMARY

A simple specific test for inner-ring o-quinones is introduced. The test consists of the reaction of the quinone with 3,4-dimethoxyaniline in hot acetic acid to give dye(s) absorbing near 600 mμ. Spot test and colorimetric modifications of the test are described. Other types of quinones and non-quinonic compounds give negative results. The spectra of the o-quinones in sulfuric acid are also presented.
With the new method, fairly specific tests are now available for (a) inner-ring p-quinones, (b) inner-ring o-quinones, and (c) terminal ring o- and p-quinones.

RÉSUMÉ

Une réaction simple et spécifique est proposée pour l'identification des o-quinones polycycliques. Elle consiste à faire réagir la quinone avec le diméthoxy-3,4-aniline.

ZUSAMMENFASSUNG

Ein einfacher und spezifischer Nachweis polycyclische o-Chinone lässt sich deren Reaktion mit dimethoxy-3,4-anilin verwenden.

REFERENCES

E. SAWICKI, T. W. STANLEY AND T. R. HAUSER, Anal. Chem., 30 (1958) 2005.
E. SAWICKI AND W. ELBERT, Chemist Analyst, 48 (1959) 68.
E. SAWICKI, T. W. STANLEY, W. ELBERT, T. R. HAUSER AND F. FOX, to be published.
E. SAWICKI, T. W. STANLEY AND T. R. HAUSER, Anal. Chim. Acta, 21 (1959) 392.
K. M. P. SINGH AND S. DUTT, Proc. Indian Acad. Sci., A8 (1938) 187.
E. BAMBERGER AND S. C. HOOKER, Ann., 229 (1885) 102.

ON THE MIXED COMPLEXES OF TETRACYCLINE METAL CHELATES

MORIZO ISHIDATE, TAKEICHI SAKAGUCHI, KIYOMI TAGUCHI AND SACHIKO KANAO

Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo (Japan)

ISHIDATE AND SAKAGUCHI[1] and SAKAGUCHI AND TAGUCHI[2] have studied the tet cycline chelates and showed that only the phenolic β-diketone group in the molec is responsible for chelate formation with metallic ions. Further investigations revea that metal chelates of tetracyclines are always cationic chelates in which the mo ratio is 1 to 1.

It seemed likely that the metallic ion in this cationic chelate retains the abil to combine with other ligands. Consequently, tetracycline chelates should tend combine further with chelating agents such as isoniazid, penicillin, etc. We ha shown that several mixed complex compounds can be prepared; these may be tern multiligand or polyligand complexes. RITTER[3] and DALE AND BENNETT[4] obtain tetracycline–metal complexes with organic acids or penicillin–aluminium–sulfa amide but no detailed information was given.

Isoniazid chelate (INAH–chelate)

FOYE AND DUVALL[5] have described INAH chelate. We have modified their pro dure slightly. Copper–INAH chelate was obtained as blue crystals, its molar ra being 1 to 1. Cobalt–INAH chelate was obtained as a light carmine-red crystall powder with a 2 to 1 ratio of ligand to metal (Table I).

A fall in pH during metal chelate formation appeared in both cases (Table Since the pH decrease with cobalt chelates appeared above pH 7 but not below p

TABLE I

Complexes	metal %		H₂O %		CT–HCl %		Formulae
	found	calc.	found	calc.	found	calc.	
INAH–Cu(II)	20.7	24.1	0	0			INAH–Cu(NO₃)
INAH–Co(II)	12.9	12.34	3.5	3.78			(INAH)₂–Co(NO₃)₂–aq.
	14.4	12.90	11.6	11.8			(INAH)₂–CoCl₂–3aq.
INAH–Cu–CT	7.55	7.16	4.26	4.06	57.0	57.9	(INAH)₂–Cu–CT–HCl–
a	7.90	7.62	5.75	6.49	65.3b	58.6	INAH–Cu–CT–HClO₄
INAH–Co–CT	7.79	7.73	6.57	7.07	65.9	68.2	INAH–Co–CT–HCl–3aq
INAH–Fe⁺³–CT	6.13	6.87	9.14	8.85	67.9	63.4	INAH–FeCl–CT–HCl–

a. Isolated at pH 4.0   b. As CT base

:ms likely that copper–INAH chelate has the structure (I) while cobalt–INAH
the equilibrium formulae shown as structures (II) and (III):

I   II   III
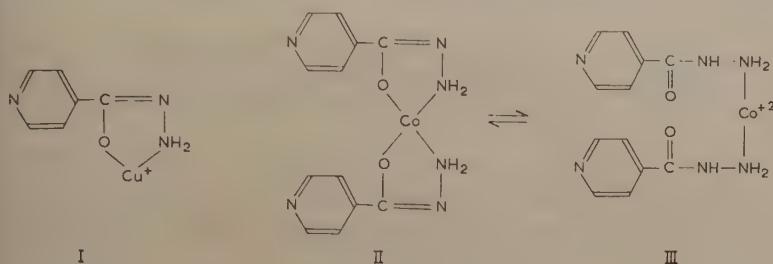
TABLE II

DECREASE IN pH IN FORMATION OF INAH CHELATES*

Metals	pH		pH after mixing	Difference
	Metal	INAH		
Cu(II)	2.79	2.79	2.68	—0.11
	4.30	4.34	3.88	—0.42
Co(II)	5.82	5.87	5.82	±0.00
	6.96	6.87	6.18	—0.69
CT–Cu(II)	2.97	2.79	2.92	+0.13
	5.11	5.03	4.44	—0.59

* Concentration of each solution was 1/200 M.

ed complex of chlorotetracycline metal with isoniazid

mixed chelate of INAH–Metal–Chlorotetracycline (CT) was obtained by adding
AH solution to an alcoholic solution of the chlorotetracycline–metal chelate.
mixed chelates formed were INAH–Fe–CT (brown precipitate) and INAH–Co–
(orange powder) which were soluble in water and hot methanol, but insoluble in
r and chloroform. Both complexes had the molar ratio of 1:1:1 (Table I).
nly IHAH–Cu–CT (yellow-green precipitate) had a molar ratio of nearly 2:1:1
it was slightly unstable on storage. In some of these cases a fall in pH drop
rred (Table II). The structure of the mixed chelate is postulated as follows:
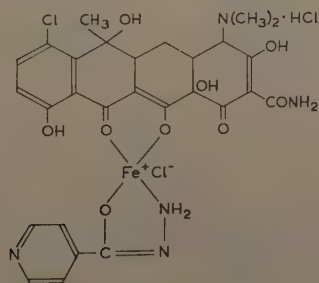
INAH –Fe –CT mixed chelate

oniazid was destroyed by ferric iron without forming any chelates but a mixed
ate of INAH–Fe–CT could be obtained if previously prepared CT–Fe chelate
added to the INAH solution.

Penicillin chelates

Penicillin G forms precipitates with several metallic ions. Only copper(II) caus[es] cleavage of penicillin[6].

Thorium(IV) forms a very sensitive precipitate from aqueous or methanolic sol[u-] tion with penicillin but not with methyl penicillin-G. This shows that the carboxyl[ic] acid group of penicillin G is important for chelate formation with metallic ions su[ch] as thorium.

On the other hand, the infrared spectrum of the cobalt–penicillin G chelate showed [a] remarkable decrease of absorbance at 1786 cm^{-1}, which was due to the β-lactam of pen[i-] cillin G (Fig. 1); this indicates that the β-lactam group is essential for chelate formatio[n.]

TABLE III

| Complexes	Metal %		H$_2$O %		CT %		Formulae
	found	calc.	found	calc.	found	calc.	
Pen. G–Th(IV)	27.33	28.70	6.41	6.67			PenG–Th(NO$_3$)$_3$–3aq.
Pen. G–Co(II)	7.86	7.74	4.46	4.74			(PenG)$_2$–Co–2aq.
Pen. G–Fe(III)	6.66	6.87	6.48	6.65			(PenG)$_2$–FeCl–3aq.
Pen. G–Th–CT	21.0	19.5	8.88	8.99	43.0	42.7	PenG–ThO–CT–HCl–6a[q.]
Pen. G–Th–DACT	22.3	21.00	8.29	8.14			PenG–ThO–DACT–5aq.
Pen. G–Fe^{+3}–CT	6.20	5.63	5.95	5.45	59.4	51.9	PenG–FeCl–CT–HCl–3a[q.]
Pen. G–Cu–CT	5.58		7.19		62.8*		at pH 6.0
Pen. G–Co–CT	5.83		4.67		67.3		at pH 6.0

* as CT base.
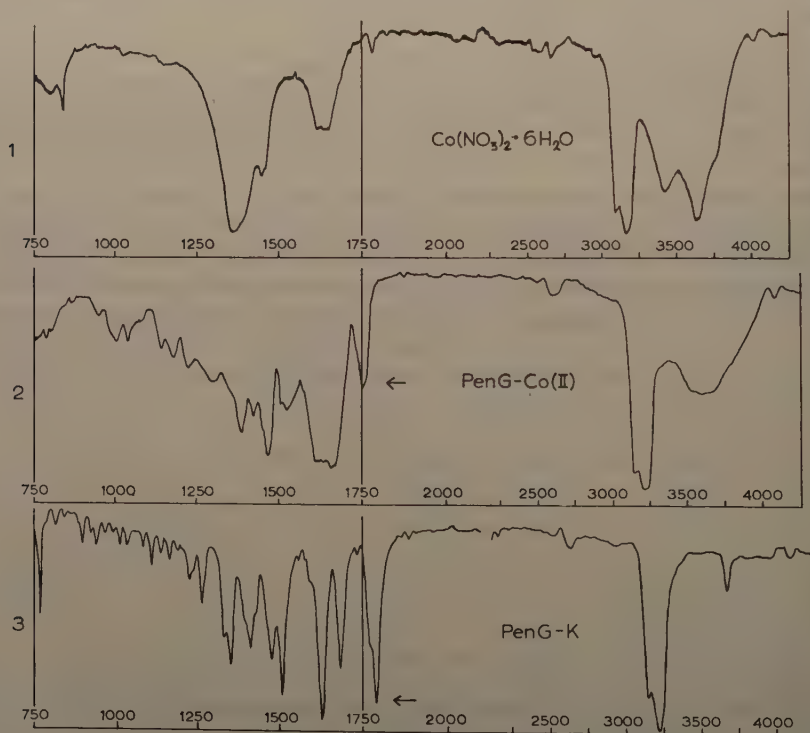
Fig. 1. Infrared spectrum of penicillin G–cobalt(II) chelate (2) compared with the componen[ts] (1 and 3). In Nujol medium with sodium chloride prism.

llysis showed that the thorium and cobalt penicillin G chelates have the molecular
nulae Pen. G–Th(NO₃)₃–3aq. and (Pen. G)₂–Co–2aq. respectively (Table III).

ed chelate of chlorotetracycline–thorium–penicillin G

he Th–CT chelate was prepared from CT–HCl and thorium nitrate solution; it
dissolved in 2 ml of water and 1 ml of an aqueous solution of penicillin G was
ed gradually. An orange-yellow powder precipitated in a short time, and was
hed with ethanol and ether and dried. It was slightly soluble in water but in-
ble in methanol, ethanol, acetone, and dioxane.
enicillin G forms a slightly soluble salt with chlorotetracycline (RUSKIN[7]). The
that desdimethylaminochlorotetracycline (DACT) is able to form a chelate with
rium (Fig. 2) proves the existence of mixed complexes even in the CT–Th–Pen. G.
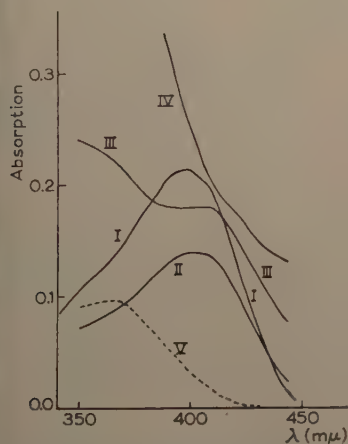
. 2. Desdimethylaminochlorotetracycline
CT) metal chelate. I. 10 μg/ml DACT–
₃OH + Th(IV), II. 10 μg/ml DACT–
₃OH + Zr(IV), III. 10 μg/ml DACT–
₃OH + UO₂(II), IV. 10 μg/ml DACT–
₃OH + Fe(III), V. 10 μg/ml DACT–
CH₃OH + —.
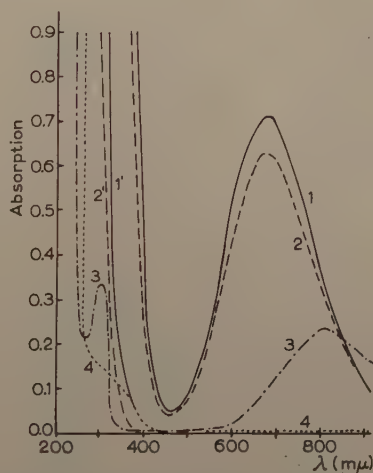
Fig. 3. Dihydrostreptomycin–Cu(II) complex
and *d*-glucosamine–Cu(II) complex. 1. DST–
Cu(II) 0.0125 *M*, pH 7.7, 1′. DST–Cu(II)
0.001 *M*, 2. Glu.–Cu(II) 0.0125 *M*, pH 7.2, 2′
Glu.–Cu(II) 0.001 *M*, 3. Cu(NO₃) 0.02, *M*,
pH 3.5, 4. DST–³/₂ H₂SO₄ 0.1 *M*, pH 7.0.

CT–thorium–penicillin G

Desdimethylaminochlorotetracycline (m.p. 157–160°) was prepared by the method
STEPHENS *et al.*[8]. It can form a chelate with thorium and other metallic ions in
same way as CT (Fig. 2).
Thorium–DACT was obtained by mixing DACT and thorium(IV) in methanolic
ition; the potassium salt of penicillin G in methanolic solution (if it does not
solve in pure methanol, a little water is added) was then added to form a precipitate
ich was dissolved in dimethylformamide. The solution was filtered and the metal
late, DACT–Th–Pen. G, was precipitated by adding ether to the solution. The

chelate could be purified by reprecipitation. The product was a yellowish powd
which was insoluble in water and alcohol (Table III).

Dihydrostreptomycin chelate (DST—chelate)

FOYE *et al.*[9] reported on the streptomycin chelates of copper, cobalt and nicke
The chelates of dihydrostreptomycin and metal ions were also studied. The chelat
were prepared by mixing dihydrostreptomycin solution with a slight excess of metall
ion solution; excess copper was removed by precipitation of the hydroxide b
adjusting the pH of the solution to 7. Ethanol was then added to give a concentratic
of less than 40% of alcohol. In the case of copper, the precipitate obtained was dee
blue (Table IV). This precipitate was soluble in water and 0.1 N potassium hydroxid
but insoluble in organic solvents. When the DST—chelate was prepared at pH 11,

TABLE IV

| Complexes | Metal % | | H₂O % | | CT—HCl %[a] | | Formulae assumed |
	found	calc.	found	calc.	found	calc.	
DST—Cu(II)	7.66	7.67	5.9	6.39			DST—Cu(HSO₄)₂—3aq.
	18.03	17.50	14.4	14.5			DST—(CuOH)₂—7aq.
DST—Ni(II)	23.1	23.6	14.0	13.8			[DST—(NiOH)₂]₂NiO—22aq.
DST—Cu—CT	8.14	7.96	8.1	8.21	66.1	64.0	DST(CT—Cu—HCl)₃—SO₄—12aq.
DST—Th—CT[c]	26.3	26.6	6.4	6.25	54.8[b]	55.0	DST(CT—ThO)₄—13aq.

[a] percent to the dehydrated samples   [b] calculated as a CT base   [c] DST—HNO₃ was us

was of a different type from that formed at pH 7; at pH 11 the chelates containe
more copper (Table IV).

The streptidine moiety of streptomycin did not form chelates below pH 7, for th
pH drop of streptidine was negative (Table V); but dihydrostreptomycin could for
a chelate in the streptidine moiety above pH 11 (Table IV).

Copper—DST chelate showed an absorption maximum at 670 mμ at pH 7.7 ar

TABLE V

DECREASE IN pH IN FORMATION OF METAL CHELATES

| Ligands | Metals | pH | | pH after mixing | Difference |
		Metal	Ligand		
DST	Cu(II)	5.10	5.20	4.75	—0.35
	Ni(II)	6.30	6.30	6.10	—0.20
	Co(II)	6.25	6.30	6.20	—0.05
	Th(IV)	3.90	3.87	3.93	+0.03
Streptidine	Cu(II)	5.20	5.20	5.28	+0.08
	Ni(II)	6.30	6.30	6.25	—0.05
	Co(II)	5.70	5.70	6.00	+0.3
	Th(IV)	3.75	3.70	3.80	+0.05
Glucosamine	Cu(II)	5.40	5.40	4.80	—0.60
	Ni(II)	6.00	6.00	5.80	—0.20
	Co(II)	6.40	6.40	6.40	±0.00
	Th(IV)	3.75	3.85	3.80	—

per–glucosamine chelate also showed a peak at 670 mμ at pH 7.2 (Fig. 3). The
ar ratio of copper–glucosamine at 650 mμ is 1 to 1 and both showed marked pH
reases below pH 7 (Table V). Therefore, it may be assumed that dihydrostrepto-
in combined with copper(II) at the N-methylglucosamine moiety in copper–DST
ate prepared at about pH 7.

ed chelates of DST-metal-CT

he affinity of copper for chlorotetracyclin is larger than that for DST, and DST
he mixed chelate tends to separate on washing with ethanol and then water.
sequently, correct analytical values for the mixed chelate with DST could not
obtained. Qualitative tests for CT[2] or DST* showed that a mixed chelate must
e been formed. The mixed chelate was prepared as follows. The copper–CT
ate was separated as mentioned above. A methanolic solution of this chelate was
n added to an aqueous solution of DST to give a concentration of 40% methanol
ess since 40% methanol did not cause any precipitation of DST. The solubility of
per–CT chelate in water decreases at pH 5–9. The mixed chelate could thus be
arated by adding excess DST solution to the copper–CT solution, and adjusting
pH to 6–7. This chelate could be washed with water and ethanol without any
ger of decomposing.

he preparation of mixed chelates suggests that enzyme processes may be clarified in
near future, for it is possible that enzyme functions are effected in mixed chelates.

SUMMARY

mixed complexes of chlorotetracycline–metal chelates with isoniazid, penicillin G, and
rdrostreptomycin were examined with Th^{+4}, Cu^{+2}, Fe^{+3}, Co^{+2}, and Ni^{+2} ions.

mechanism is proposed that accounts for the formation of the mixed complexes; cationic
ates of tetracycline have a molar ratio of 1 : 1 of metal to chlorotetracycline and mixed com-
es are formed by combining with other ligands through the remaining covalencies. The
erties and preparation of the mixed complexes are given.

RÉSUMÉ

auteurs ont effectué une étude sur les complexes et les chélates formés entre la chloroté-
ycline, quelques cations (Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4}) et les trois composés suivants: isonia-
, pénicilline G et dihydrostreptomycine.

ZUSAMMENFASSUNG

wird eine Untersuchung beschrieben über die Bildung und Eigenschaften der Komplexe, die
Chlorotetracyclin–Metallchelaten, Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4} mit Isoniazid, Penicillin G
Dihydrostreptomycin entstehen.

REFERENCES

. ISHIDATE AND T. SAKAGUCHI, *Pharm. Bull. (Tokyo)*, 3 (1955) 147.
. SAKAGUCHI AND K. TAGUCHI, *Pharm. Bull. (Tokyo)*, 3 (1955) 303.
. RITTER, *U.S. Pat.* 2, 736, 725; *C. A.*, 50 (1956) 10348.
 K. DALE AND M. E. BENNETT, *U.S. Pat.* 2, 752, 335; *C. A.*, 50 (1956) 15029.
. O. FOYE AND R. N. DUVALL, *J. Am. Pharm. Assoc., Sci. Ed.*, 47 (1958) 285.
. GÜNTHER, *Pharmazie*, 5 (1950) 577; *C. A.*, 45 (1951) 7566.
 L. RUSKIN, *Brit. Pat.* 772, 573; *C. A.*, 51 (1957) 10848.
 R. STEPHENS, L. H. CONOVER, R. PASTERNACK, F. A. HOCHSTEIN, W. T. MORELAND, P. P.
EGNA, F. J. PILGRIM, K. J. BRUNINGS AND R. B. WOODWARD, *J. Am. Chem. Soc.*, 76 (1954)
68.
. O. FOYE, W. E. LANGE, J. V. SWINTOSKY, R. E. CHAMBERLAIN AND J. R. GUARINI, *J. Am.
harm. Assoc., Sci. Ed.*, 44 (1955) 261.

lfosalicylic acid–oxine–NaOH–NaOBr or diacetyl-β-naphthol reaction.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBON

IN TOBACCO SMOKE

A. CANDELI*, A. J. LINDSEY AND K. PERSAUD

Sir John Cass College, Department of Chemistry, London (Great Britain)

INTRODUCTION

This paper deals with the application of the recent improved method[1] for determini polycyclic aromatic hydrocarbons to tobacco smoke and also describes improvemen in the apparatus and technique formerly used[2,3]. A very wide interest has be shown in the amounts of polycyclic aromatic hydrocarbons in tobacco smoke becau of the known carcinogenic action of some of these compounds, and the prese method has been developed to expedite the analysis as much as possible. Oth developments are also discussed.

EXPERIMENTAL

Apparatus

The smoking apparatus is a development of that formerly described[3], and is shown in Fi which, apart from the suction device is drawn to scale. Interconnection between the various pa of the apparatus is standardised to allow rapid replacements and rearrangements and is m with B19 joints. All containers have B24 connectors. As far as possible standard equipment norm
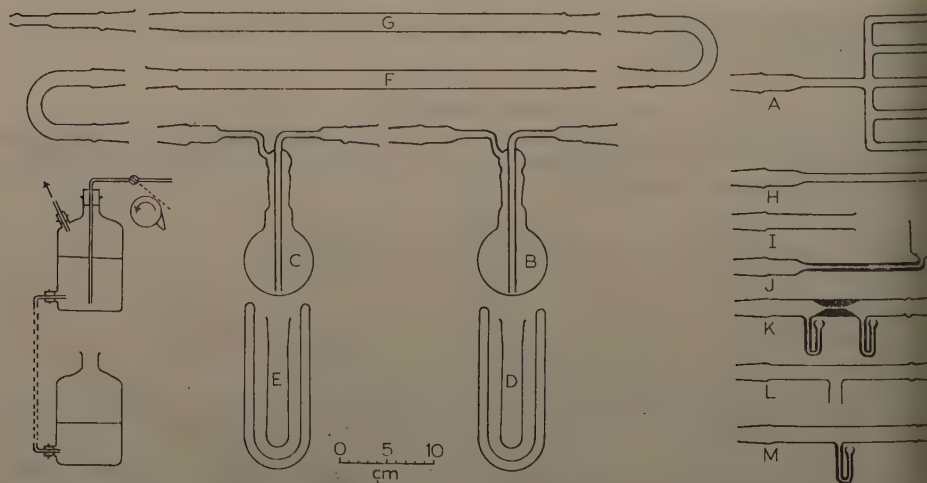

Fig. 1. The smoking apparatus.

---

* Present address: Instituto d'Igiene dell'Universita di Perugia, Italy.

…ked by apparatus suppliers has been used. The collection flasks B, C, are used for solvents or
…be replaced by cold traps D, E. The two colums F, G, filled with 3 mm glass balls, and used
…njunction with the flasks are capable of trapping all the smoke from five cigarettes simultane-
…w smoked without cold traps. All these parts are secured to a board with Terry clips. Multiple
…ers, A, to take five cigarettes were normally employed but larger ones have been used.
…ever, smoking with holders taking more than ten cigarettes is difficult to control. Single
…rette holders H, cigar holders I, and pipes J, are all readily plugged in to this equipment, and
…llary equipment such as flowmeters K, thermometer or thermocouple ports L, and manom-
…s M, can also be added. Suction pressures and times are controlled by the distance between
…aspirator levels and the length of the cam used to open the stopcock. Although some workers
…er to use constant volume suction[4-6], it is especially convenient to use constant pressure
…ion for systems in which the interchange of various smoking and collecting devices may be
…lled. Once the conditions have been standardised by means of a flowmeter and manometer,
… method of smoking is in all respects as satisfactory as any other.

…oking and analytical technique for cigarettes

…ll materials and apparatus should be purified and cleaned as described pre-
…usly[1].

…he simplest technique for analysis of cigarette smoke is to use about 500 ciga-
…tes; to smoke them in a multiple holder with spectroscopically pure cyclohexane in
… flasks and with the timing and suction adjusted to suit the type of smoking
…bit it is desired to imitate. In Great Britain for normal size cigarettes (7 cm long
…d 0.8 cm diameter) the average type of smoking corresponds to puffs of 2 seconds
…ration with suction pressure equal to 25 cm of water. With these conditions
…oking to a stub length of 1.5 cm requires a total smoking time of about 12 min.
…he cyclohexane is poured off after the smoking is over and the whole apparatus
…cluding the flasks) extracted with hot acetone. Cyclohexane soluble compounds
…e then removed from the acetone solution by the following process. The acetone
…ution is reduced to about 50 ml, mixed with an equal volume of cyclohexane, and
…e mixture distilled until the temperature of the vapour reaches 72°. It is then
…owed to cool, the cyclohexane poured off from the semi solid residue and this is
…en repeatedly heated with several quantities of cyclohexane each of which is poured
… in turn. All these solutions combined are worked up separately from the original
…clohexane solution as follows.

…The cyclohexane solutions are shaken in turn three times with 2 N sulphuric acid,
…ater, 2 N sodium hydroxide and finally again with water until the washings are
…utral. The neutral cyclohexane solutions are dried with anhydrous calcium chloride
…d separately reduced to small volume (10 ml). Sometimes stubborn emulsions are
…rmed during the washing processes but they can be broken by adding potassium
…loride.

…The solution in cyclohexane is placed on a large column of active alumina (10–
…5 cm) (Peter Spence, type H, 100 to 200 mesh), eluted with cyclohexane and col-
…ted in 3-ml fractions. Selected fractions throughout the sequence are examined in
…e D.K.2 U.V. recording spectrophotometer between 250 and 500 mµ. The fractions
…e diluted if necessary to give spectra with suitable absorption at the lower wave-
…gths. Generally about 200 fractions are collected. Automatic collection of fractions
…preferable in order to ensure even distribution of components in the sequence. The
…ject of examining the fractions in this preliminary chromatography is to select
…ups of fractions for combination in later chromatographic separations in order to
…regate the compounds to be determined. The eluates in selected groups (generally

two or three) of fractions are combined, distilled to small bulk (10 ml) in a water ba[th]
and rechromatographed on alumina columns of two activities (5 ml on each) to facil[i]-
tate recognition of individual compounds in the chromatographic series. The alumin[a]
activities recommended are those formerly found suitable to space the compoun[ds]
evenly in the sequence[1], that is in equilibrium with the vapour of either 50% or 70[%]
sulphuric acid. These later columns are smaller and the size is best determined b[y]
a preliminary experiment. More complete separations can be effected by repeatin[g]
the separations on additional small columns, but it should be noted that losses occu[r]
with each successive chromatographic process.

DISCUSSION

With tobacco smoke fractions a great deal of absorption is observed in the ultra-viol[et]
and most of this is due to other neutral compounds than the polycyclic aromat[ic]
hydrocarbons. This makes it necessary to use the "baseline" technique[1], for quant[i]-
tative work. It is also important to complete the analysis as soon as possible becau[se]
of possible losses of hydrocarbons during storage in solution.

Other investigators[6-12], have commented upon the difficulties of detecting a[nd]
measuring amounts of these compounds totalling only to a few parts per million [in]
the presence of other highly absorbing neutral components and have proposed a[nd]
used various ways of overcoming the difficulties.

The most complete identifications were those of VAN DUUREN[7] who, commencin[g]
with 4 kg of smoke condensate (corresponding to 174,000 cigarettes), after chromato[g]-
raphy on a large scale isolated the mixed picrates of the polycyclic aromatic hydr[o]-
carbons in impure form. TARBELL's paper chromatographic method[13] was used [to]
isolate the pure hydrocarbons. The spots, recognised in ultra-violet light were c[ut]
out, redissolved, and identified by their ultra-violet spectra. The merit of the meth[od]
is in the unmistakable identification of the complete spectra, but the yields were l[ow]
and to an undefined extent so that it could in no sense be called quantitative. T[he]
length of the process and the large quantities required also make it impossibly tedio[us]
for repetitive and comparative work.

Even larger scale experiments of WRIGHT[14] have given pure products, and pu[re]
crystals of 3,4-benzpyrene and other hydrocarbons were first obtained from tobac[co]
smoke in his laboratory. The smoking process corresponded more to pipe smoki[ng]
than cigarette smoking and the yields were not quantitative. Crystalline sampl[es]
of 3,4-benzpyrene have also been obtained by HOFFMAN[15] from cigarette smoke.

Fluorescence spectroscopy was employed to confirm the first determinations [of]
3,4-benzpyrene in tobacco smoke[16], and has since been used by several workers as [a]
detecting and determining process. BENTLEY AND BURGAN[6] prefer fluorescen[ce]
spectroscopy to ultra-violet methods for determinations, but HOFFMAN A[ND]
WYNDER[15] regard it solely as confirmatory of identity and not so accurate as U.[V.]
spectroscopy for quantitative work because of quenching effects. LATARJET et al[.]
also use a sensitive fluorescence method for determinations. The variation in report[ed]
amounts of 3,4-benzpyrene (which is still the most potent carcinogen found [in]
tobacco smoke) vary between about 1 to 18 micrograms in the mainstream smo[ke]
from 100 cigarettes. If one single investigation[10] is not included most determinatio[ns]
lie between 1 to 3 micrograms and, when variations of smoking method and analyti[c]

nniques are considered and also the possibility of losses during separation, this
st be considered good agreement.

f all the methods, the present, which employs the technique of elution chromatog-
hy with two activities of alumina, is most convenient and rapid, and is specially
sfactory for comparisons because it requires only a few hundred cigarettes for
h determination.

ACKNOWLEDGEMENTS

SUMMARY

provements have been described in the apparatus and methods employed in determining
cyclic aromatic hydrocarbons in tobacco smoke by alumina-column chromatography and
omatic ultra-violet spectrophotometry.

RÉSUMÉ

; perfectionnements ont été apportés à l'appareillage et aux méthodes utilisés pour le dosage
hydrocarbures aromatiques polycycliques dans la fumée de tabac.

ZUSAMMENFASSUNG

wird eine verbesserte Apparatur und Methode beschrieben zur Bestimmung polycyclischer
matischer Kohlenwasserstoffe im Tabakrauch.

REFERENCES

A. J. LINDSEY, Anal. Chim. Acta, 20 (1959) 175; 21 (1959) 101.
B. T. COMMINS, R. L. COOPER AND A. J. LINDSEY, Brit. J. Cancer, 8 (1954) 296.
R. L. COOPER AND A. J. LINDSEY, Brit. J. Cancer, 9 (1955) 304.
J. A. BRADFORD, W. R. HARLAN AND H. R. HANMER, Ind. Eng. Chem., 28 (1936) 836.
W. G. ILES AND C. F. SHARMAN, J. Appl. Chem., 7 (1957) 384.
H. R. BENTLEY AND J. G. BURGAN, Analyst, 83 (1958) 442.
B. L. VAN DUUREN, J. Nat. Cancer Inst., 21 (1958) 1.
S. NEUKOMM, Oncologia, 10 (1957) 137.
M. J. LYONS, Nature, 177 (1956) 630.
S. Z. CARDON, E. T. ALVORD, H. J. RAND AND R. HITCHCOCK, Brit. J. Cancer, 10 (1956) 485.
R. LATARJET, J. L. CUZIN, M. HUBERT-HARBART, B. MUEL AND R. ROYER, Bull. Assoc. franç.
étude cancer, 43 (1956) 180.
A. I. KOSAK, J. S. SWINEHART AND D. TABER, J. Nat. Cancer Inst., 17 (1956) 375.
D. S. TARBELL, E. G. BROOKER, A. VANTERPOOL, W. CONWAY, C. J. CLAUS AND T. J. HALL,
J. Am. Chem. Soc., 17 (1955) 767.
G. F. WRIGHT, Proc. Third Nat. Cancer Conf., (1957) 479 and personal communication.
D. HOFFMAN AND E. L. WYNDER, personal communication.
R. L. COOPER, A. J. LINDSEY AND R. E. WALLER, Chem. & Ind., (1954) 1418.

THE DETERMINATION OF TANTALUM AND TUNGSTEN IN ROCK
AND METEORITES BY NEUTRON ACTIVATION ANALYSIS

D. H. F. ATKINS AND A. A. SMALES

Atomic Energy Research Establishment, Harwell (Great Britain)

INTRODUCTION

In the past the determination of trace quantities of tantalum and tungsten in rock and other materials with a complex matrix has been hampered by the lack of suitab analytical methods. While methods for the determination of these elements on th microgram scale are available, determinations at the sub-microgram level are difficul particularly with tantalum where the utilisation of a chemical property in the fin stage of the estimation frequently necessitates a separation from niobium.

RANKAMA[1], in his comprehensive study of the geochemistry of tantalum, avoide a separation from niobium by determining the element by X-ray spectrography aft enrichment of the mixed earth acids by phenyl arsonic acid precipitation and separ tion from titanium by digestion with salicylic acid.

The abundance of tungsten in igneous rocks has been investigated by SANDELI Rock samples were dissolved in mixed acids and a double sodium hydroxide precipit tion was used to remove iron and titanium. Molybdenum was precipitated wi hydrogen sulphide and tungsten determined colorimetrically as the lower valen thiocyanate after ether extraction. Large quantities of vanadium interfere in th determination. More recently VINOGRADOV *et al.*[3] have published the results of systematic investigation of the tungsten and molybdenum contents of various roc using a spectrochemical method. Samples of the rock were fused with sodium carbo ate and the melt extracted with water, acidified with hydrochloric acid and tungst and molybdenum co-precipitated with tannin and methyl violet. The precipitate w separated, dried and ignited and tungsten and molybdenum determined spectr graphically in separate portions of it.

A number of reviews of the technique of radioactivation analysis have be published[4,5] and the application of the method to materials of geochemical intere is exemplified by the work of CABELL AND SMALES[6]. Briefly the chief advantages the technique lie in its freedom from blank difficulties and from contamination err after irradiation and, since an inactive isotopic carrier is added before the samp is processed chemically, chemical separations at the microgram level are avoided.

The method of neutron activation analysis is insensitive to natural niobium a in consequence it is a particularly valuable technique for the determination of ta talum. KOHN[7] has described the direct determination of tantalum in ferro–niobiu

ll niobium ores, and LONG[8], BEYDON AND FISHER[9] and EICHOLZ[10] have also
scribed methods for the determination without chemical separation. A chemical
aration for the mixed earth acids was used by MILNER AND SMALES[11] in the deter-
nation of niobium in stainless steel. Conventional steps were used to isolate the
ides from the steel and following irradiation together with tantalum pentoxide
ndards tantalum in the mixture was determined by gamma spectrometry.
BROOKSBANK, LEDDICOTTE AND REYNOLDS[12] have used neutron activation analysis
determine tungsten and other impurities in titanium, and tungsten has been deter-
ned in silicon by JAMES AND RICHARDS[13]. A method using a low level radium-
ryllium neutron source has been described by HUARINGA[14] and LELIAERT et al.[15,16]
ve used low level neutron source in the determination of tungsten in high alloy
els both with and without chemical separation.

A more generally applicable method for the determination of tantalum and
ngsten has now been developed and is described in this paper. The method has been
plied to the analysis of some iron and steel standards, rocks from the Skaergaard
trusion of East Greenland, the standard granite G1 and diabase W1 and some
ony and iron meteorites.

NUCLEAR DATA

ble I contains a list of some nuclear characteristics of the nuclides produced by
ermal neutron irradiation of tantalum and tungsten, and the activities induced
them by irradiation in the Harwell Pile (BEPO) for one month. The greatest
nsitivity in the estimation is found with the nuclides ^{182}Ta and ^{187}W, and assuming

TABLE I

NUCLEAR DATA FOR TANTALUM AND TUNGSTEN

Target isotope	Abundance in natural element (%)	Isotopic activation cross-section (barns)	Product on neutron activation	Radiation and energy (MeV)	Half-life	Activity d/m/μg after 7 days in BEPO
$^{180}_{73}$Ta	0.012	—	^{181m}Ta ^{181}Ta	Isomeric transition stable	0.33 sec	—
$^{181}_{73}$Ta	99.988	0.07 22	^{182m}Ta ^{182}Ta	Isomeric transition β⁻ 0.514, 0.44, 0.36 γ 1.22, 1.12 and others	16.5 min 115 days	1.4·10⁴ 7·10⁵
$^{180}_{74}$W	0.14	<20	^{181}W	Electron capture γ 0.132, 0.136	145 days	7·10²
$^{182}_{74}$W	26.2	0.5 20	^{183m}W ^{183}W	Isomeric transition stable	5.5 sec	2.6·10⁴
$^{183}_{74}$W	14.3	11	^{184}W	stable		
$^{184}_{74}$W	30.7	— 2	^{185m}W ^{185}W	Isomeric transition γ 0.165, 0.130 β⁻ 0.430	1.6 min 75.8 days	— 3·10³
$^{186}_{74}$W	28.7	36	^{187}W	β⁻ 1.33, 0.63, 0.34 γ 0.68 and others	24 h	2·10⁶

8 h for chemical processing, a 50% chemical yield and finally beta-counting with conventional counter, a limit of detection of 10^{-10} g for tantalum and 10^{-11} g f tungsten is possible. In practice adequate sensitivity was usually obtained wit irradiation periods of 36 h. The chemical separation was designed to isolate the shor half-life (24 h) tungsten before 115 day half-life tantalum.

EXPERIMENTAL

Irradiation

Samples and standards were weighed into clean, dry silica ampoules prepared from thin walled silica tubing of 4-mm internal diameter[17]. The ampoules were sealed an samples and standards were packed together into an aluminium can and irradiate in the "self-serve" position in BEPO. Rock samples and stony meteorites were groun to pass a 100-mesh B.S. sieve. Iron meteorites and standard iron and steel sample were irradiated as turnings or single pieces of the metal. The preparation of sample for irradiation is discussed in some detail below.

Standards

Both tantalum and tungsten have appreciable neutron capture cross-sections i the thermal region of the pile neutron spectrum (Ta = 22 barns, W = 18 barns) an in addition, both elements show resonance peaks of more than 10,000 barns in th intermediate or epithermal region of the spectrum[18]. As a result the possibility o self-shielding during irradiation, leading to a reduction of the effective neutron flu through a sample and causing unequal activation of samples and standards, canno be neglected. To investigate this phenomenon varying weights of the pure oxide of tantalum and tungsten were irradiated simultaneously in BEPO and the induce specific activities were determined (Table II). The results show a decrease in specifi activity with increase in sample weight (indicative of self-shielding) and illustrat the unsuitability of pure tantalum and tungsten compounds as standards in th determination.

The effect of self-shielding may be overcome by diluting the absorbing elemen with material of low cross-section, such as water, silica, alumina or sucrose. Homo geneous solid dilutions are difficult to prepare and a series of aqueous dilutions wer made and investigated. Sealed silica ampoules containing dilutions of tantalum a

TABLE II

SELF-SHIELDING EFFECTS IN THE IRRADIATION OF SOLID TANTALUM AND TUNGSTEN OXIDES

Weight Ta_2O_5 (mg)	Specific activity counts per minute per mg Ta	Weight WO_3 (mg)	Specific activity counts per minute per mg W
2.7	121000	1.9	72400
5.8	113500	4.0	66500
14.9	112500	11.5	63500
19.8	111000	14.3	62300
25.7	109000	19.8	62500
30.6	108500	25.4	60200
38.3	107500	36.7	56500
40.6	105000	40.3	59200
55.1	103000	48.3	57900

oxalate complex in oxalic acid solution and tungsten as ammonium tungstate in
ite ammonia were irradiated and the specific activity determined (Table III).

TABLE III

F-SHIELDING EFFECTS IN THE IRRADIATION OF DILUTE SOLUTIONS CONTAINING TANTALUM AND
TUNGSTEN

Weight mg Ta per g solution	Specific activity counts per minute per mg Ta	Weight mg W per g solution	Specific activity counts per minute per mg W
6.09	$5.81 \cdot 10^3$	0.485	$55.5 \cdot 10^3$
6.09	$5.92 \cdot 10^3$	0.485	$54.8 \cdot 10^3$
2.44	$5.97 \cdot 10^3$	0.0245	$53.3 \cdot 10^3$
2.44	$5.88 \cdot 10^3$	0.0245	$52.8 \cdot 10^3$
0.609	$5.95 \cdot 10^3$	0.00245	$57 \cdot 10^3$
0.0609	$5.95 \cdot 10^3$		

No significant change in activity was detectable over the range of dilutions examined,
ll solutions containing tungsten and tantalum at lower concentrations than the
ximum considered in Table III were used in this work. The neutron capture cross-
ttions of the sample matrix materials, mainly silica or iron, for the pile flux spec-
um are sufficiently low for this phenomenon to be neglected with the small sample
ights employed.

Fresh liquid standards were prepared on alternate weeks by dilution of gravimetric-
y standardised carrier solutions with oxalic acid solutions prepared from deminer-
sed water. In practice mixed standards containing both tantalum and tungsten
re irradiated and after irradiation subjected to the full chemical separation and
rification procedure. Standard solutions for irradiation contained appreciable
antities of oxalic acid, essential to stabilise the tantalum oxalate complex, and it
s necessary to investigate the possibility of "blank" contributions brought about
traces of tantalum and tungsten present in this compound. Analysis of the batch
oxalic acid used throughout the work gave a tantalum content of 0.0005 p.p.m.
d a tungsten content of 0.05 p.p.m. Contributions from this level of impurity could
neglected.

ssolution

The methods employed to bring the irradiated samples into solution in the presence
carriers were dependent on the nature of the sample. Rocks and stony meteorites
re brought into solution by sintering with sodium peroxide for 10 min at 480
20°[19], in a nickel crucible of 5-ml capacity. Mineral acid mixtures containing
drofluoric acid were used for iron meteorites and iron and steel samples.

tline of the radiochemical procedure

A number of radiochemical procedures for tantalum and tungsten have been de-
ibed[20,21] including one for the separation of tungsten from a tantalum target[21].
e latter method utilises the ethyl acetate extraction of stannous chloride reduced
ngsten thiocyanate and isolates tungsten rapidly and in good yield. This method
s investigated initially when, after extraction of tungsten, difficulties were expe-
nced in separating tantalum cleanly from the aqueous phase containing several

times its weight of tin and boric acid. Tantalum yields were found to be less errati[c] when zinc dust was substituted for stannous chloride as reducing agent but th[e] procedure was still slow and tedious. The method adopted and used for most of th[e] work was based on the technique of STEVENSON AND HICKS[22] for the di-isopropy[l] ketone (DIPK) extraction of tantalum from solutions 0.4 M in hydrofluoric acid an[d] 6 M in sulphuric acid. Using a radiochemical procedure based on this method thes[e] authors claim decontamination factors of better than 10^5 for tantalum from fissio[n] products. Partition coefficients for tungsten under conditions of maximum tantalu[m] decontamination were determined and found to be 0.1. Subsequently supplies o[f] DIPK failed and methyl isobutyl ketone (hexone) was substituted for it in the extra[c]tion[23]. Using identical conditions of acidity, partition coefficients for the tungste[n] extraction of 0.07 were obtained. Any niobium associated with tantalum in th[e] samples will follow tungsten in the separation whether DIPK or hexone is used a[s] solvent.

Solutions of a number of complexing agents for the back extraction of tantalu[m] from the organic phase after separation were considered. Solutions of oxalic, tartari[c] citric and lactic acids, hydrochloric acid–boric acid mixtures, water and hydroge[n] peroxide solutions of varying concentration were investigated. Five per cent v/[v] hydrogen peroxide was found to be the most satisfactory reagent, one extraction bein[g] sufficient to recover the tantalum where the organic phase was DIPK, hexon[e] requiring two.

Procedures for source mounting tantalum as its oxide prior to β-counting hav[e] been described[20,21], but the process requiring a high temperature ignition stage t[o] dehydrate the oxide and subsequent grinding to obtain the oxide in a suitabl[e] powdered form for spreading on a counting tray, was inconvenient. A search for a[n] alternative compound was made and the material eventually selected was tri-2,2[-] dipyridyl ferrous fluorotantalate, $Fe(dipy)_3(TaF_6)_2$, where (dipy) is 2,2'-dipyridyl[24,2] The thermal stabilility, solubility in hydrofluoric acid and dependence of the const[i]tution of the compound on the acid strength of the precipitating medium had n[ot] been described and were investigated. The compound was found to be thermall[y] stable at temperatures of up to 200°, to have a minimum solubility at room temper[a]tures of 23 mg per 100 g in 0.1 N hydrofluoric acid and its composition was indepe[n]dent of acid strength when precipitated in solutions of up to 18 N hydrofluoric ac[id] concentration. The compound was not hygroscopic. Despite its relatively high solubil[i]ty the material was found to fulfil satisfactorily the requirements of a source f[or] beta-counting.

Procedures for mounting tungsten as the compound with 8-hydroxyquinoline and the oxide[21] have been described. The same objections to the use of the oxi[de] apply as in the case of tantalum pentoxide and the oxinate was used in this wor[k.] Precipitation was carried out in hot neutral or slightly alkaline solution and w[as] followed immediately by acidification with acetic acid.

The method finally adopted for the isolation and radiochemical purification of th[e] elements may be outlined as follows. Samples and standards are taken into soluti[on] in the presence of carriers and tantalum and tungsten co-precipitated by tannin an[d] cinchonine. The precipitate is removed by filtration, washed with 2% ammoniu[m] chloride solution and treated with nitric and sulphuric acids to destroy organ[ic] matter. Nitric acid is removed by fuming with sulphuric acid and the mixed hydrat[e]

les precipitated by the addition of water to the cooled sulphuric acid solution.
oxides are dissolved in a solution 0.4 M in hydrofluoric acid and 6 M in sulphuric
and tantalum removed by solvent extraction with DIPK or hexone.
ungsten is recovered from the aqueous phase and freed from traces of the solvent
digestion with nitric acid. The precipitated oxide is washed and put through a
es of ammonia/nitric acid cycles before being mounted for counting as the oxinate.
antalum is backwashed from the organic phase with 5% hydrogen peroxide and
rated tantalum pentoxide precipitated with ammonia. The extraction cycle is
ated, and finally the hydrated oxide is dissolved in the minimum volume of
rofluoric acid before precipitation as tri-2,2'-dipyridyl ferrous fluorotantalate
measurement of the induced activity present.

asurement of radioactivity

he activity present in the sources prepared for counting was measured by either
a- or gamma-counting. A conventional end-window Geiger counter assembly was
d for beta-counting. Gamma activities were measured and the spectra of [182]Ta and
V recorded with the aid of a 100 channel, sodium iodide crystal, scintillation
trometer.

antalum emits beta particles of maximum energy 0.53 MeV and 80% of the beta
ticles emitted by [187]W have a maximum energy of 0.63 MeV. It was necessary
refore, to investigate whether corrections to the observed counting rates caused
self-absorption of the beta particles emitted by the source materials were applic-
. The effect of self-absorption was determined by preparing sources of varying
ckness from common stocks and recording the apparent specific activities (Table
. In practice sources of between 10 and 15 mg per square centimetre were used,
while the effects for [187]W within this range could be neglected, corrections for
Ta were appreciable.

TABLE IV

LF-ABSORPTION AND SCATTERING EFFECTS IN TANTALUM AND TUNGSTEN SOURCE MATERIALS

Tungsten oxinate		Tri-2,2-dipyridyl ferrous fluorotantalate	
Source wt. (mg per sq.cm)	Counts per minute per mg	Source wt. (mg per sq.cm)	Counts per minute per mg
1.67	97	1.68	120
2.20	103	2.93	126
3.43	109	4.00	125
5.20	110	6.27	123
7.30	108	7.67	117
8.51	110	8.82	116
10.75	102	9.45	116
14.42	99	13.32	105
18.17	93	17.48	98

estigation of radiochemical purity

hree checks on the radiochemical purity of the final sources are applicable,
nely: the construction of decay curves for the radioactivity emitted by the nuclide;
ermination of the maximum beta particle energy and comparison of the general
pe of the beta absorption curves with those obtained from standards of known radio-

chemical purity; examination of the gamma ray spectrum. The construction of dec
curves and beta absorption curves is facilitated by the availability of automa
counting equipment, and the gamma spectra of relatively weak sources of activ
may be readily obtained with multi-channel gamma spectrometers. The applicat
of two of these checks is usually sufficient to indicate the radiochemical purity
the source.

Decay curves for ^{187}W ($t_{\frac{1}{2}} = 24$ h) were always recorded and if sufficient rad
activity was present in the source, as was almost invariably the case, the decay v
followed for at least five half-lives (Fig. 1). Gamma spectra, using a 100-chan
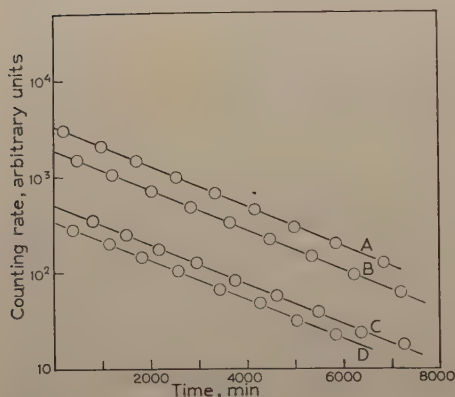

Fig. 1. Decay curves for ^{187}W (half-life 24 h).
Curves A and B standards. Curves C and D
Skaergaard Intrusion Sample E.G. 4327.
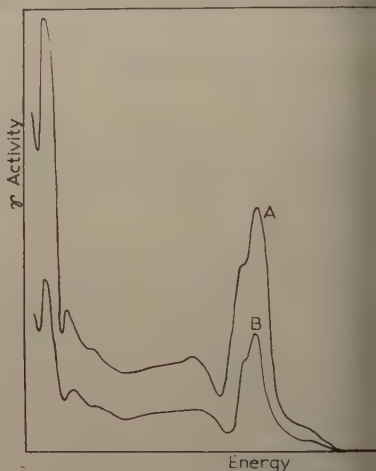

Fig. 2. Gamma spectra for ^{182}Ta.
standard; B, sample G1.

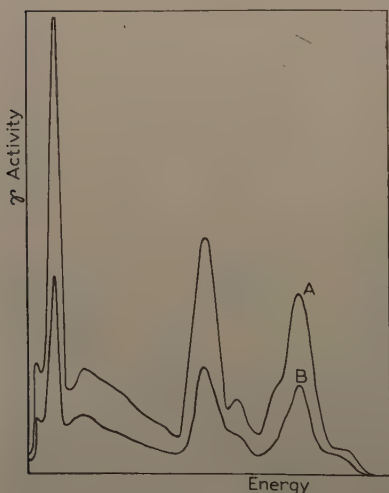Fig. 3. Gamma spectra for ^{187}W. A,
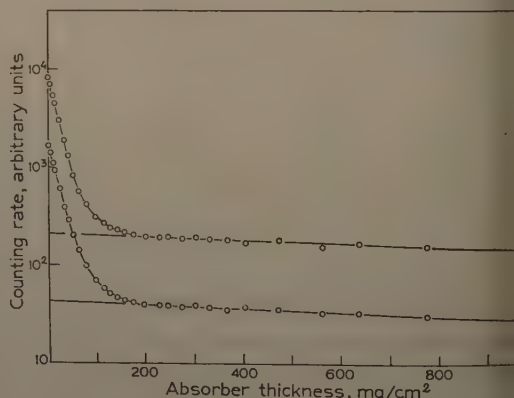standard; B, sample G1.

Fig. 4. Absorption curves for ^{182}Ta. Curve A, st
ard; curve B, ^{182}Ta from sample G1.

trometer, were constructed and compared with those obtained from the standards
the determination for both tantalum and tungsten (Figs. 2 and 3). The half-life of
$t_{\frac{1}{2}} = 115$ days) is too long for a decay curve to be prepared as an adjunct to a
ine determination and as additional confirmation of the radiochemical purity
is nuclide beta absorption curves may be prepared (Fig. 4).

METHOD

iminary treatment of silicate materials

the sample for analysis consists of silicate material grind it as finely as possible,
ertainly to less than 100 B.S. sieve size. Weigh suitable amounts (usually 40–80
into clean, dry silica ampoules and seal the tubes. Mark the ampoules with paint
pack into 3" aluminium BEPO cans together with standards for irradiation in
PO. After irradiation allow two hours for the short lived activities to decay
re bringing the can back to the laboratory in a shielded container. Carry out the
al operations of the chemical separation behind lead shielding. The number of
ations necessarily performed in this way will depend on the nature of the sample
its irradiation period.

pen the sample ampoules and carefully transfer the contents to a nickel crucible
ml capacity containing a layer of sodium peroxide. Thoroughly mix the contents
he ampoules with the sodium peroxide using a nickel spatula, cover with a further
r of sodium peroxide and place for 10 min in a furnace maintained at 480°
o°. Remove the crucible and cool rapidly by dipping the outside in water. Invert
crucible and tap the base to detach the sinter cake. Transfer the cake to a 250-ml
ker containing 35 mg of tantalum as the oxalate complex, 35 mg of tungsten as
um tungstate, 10 ml of 20% tartaric acid and 70 ml of distilled water containing
of ammonium chloride. As soon as the initial violent reaction has abated rinse the
el crucible, add the washings to the beaker and acidify with 10% v/v sulphuric
. A clear solution should be obtained at this stage. Boil the weakly acid solution
add ammonia dropwise until it is just alkaline followed by 50% hydrochloric
until the solution is acid and then two drops in excess. Add 50 ml of hot 2%
in solution slowly and with constant stirring and boil gently to coagulate the
ipitate before removing from the hot-plate. Add 10 ml of 5% cinchonine in 25%
rochloric acid to the hot solution slowly and with constant stirring and leave to
d for at least thirty minutes before filtering through an 11-cm Whatman No. 541
r paper. Wash the precipitate with hot 2% ammonium chloride solution and
ard the washings.

iminary treatment of iron material

etallic samples and iron meteorites are usually supplied as turnings or small
es cut from the parent sample. As the tools used in preparing the samples fre-
tly contain high concentrations of tungsten, the possibility of surface contamina-
of the sample cannot be ignored and must be eliminated by cleaning. Briefly
the samples with dilute hydrochloric acid containing a little hydrogen peroxide,
thoroughly with demineralised water and finally with acetone before drying.
gh 50–100 mg of the samples into clean, dry silica ampoules, seal and pack into 3"
inium BEPO cans and irradiate together with standards. When the irradiation

has been completed dissolve the metallic samples in the presence of carriers, tartar
and hydrofluoric acids, the acids used for dissolution depending on the sampl
During dissolution a little oxidising agent (nitric acid) is added, if not already presen
to re-oxidise any reduced tungsten. After the necessary adjustments to the acidi
and the addition of 5 g of ammonium chloride, tantalum and tungsten are precipitat
is above.

Preliminary treatment of standards

Transfer duplicate small volumes of the standard solution to clean, weighed sili
ampoules. Centrifuge to deposit the solution at the lower end of the ampoule, wei
and seal. Irradiate standards and samples together. The standard solutions employ
usually contain higher concentrations of tantalum and tungsten than the sampl
and to avoid the possibility of cross contamination it is advisable to process th
samples, at least to the separation stage, before dealing with the standards.

Centrifuge the standard ampoules and open carefully to prevent losses caused l
the build up of pressure during irradiation. Remove the solution with a droppi
pipette, rinse the last traces of standard from the inside of the ampoule with war
dilute oxalic acid solution and transfer the mixed standard and washings to a 250-
beaker containing tantalum and tungsten carrier solutions and tartaric acid.

From this stage the chemistry performed for the separation and isolation of ta
talum and tungsten from the standards is identical with that used for the sampl

Separation

Transfer the washed tannin-cinchonine precipitate of tantalum and tungsten
a 250-ml beaker and add 20 ml of concentrated nitric acid and 5 ml of concentrat
sulphuric acid. Heat on the hot-plate until all the organic material is destroye
adding more nitric acid when necessary. Fume to remove excess of nitric acid. C
and precipitate the hydrated oxides of tantalum and tungsten by the addition
50 ml of demineralised water. Add 5 ml of concentrated hydrochloric acid, boil, a
and spin in a centrifuge to remove the oxides. Treat the precipitate with 10 ml of
solution 0.4 M in hydrofluoric acid, and 6 M in sulphuric acid, rejecting any insolul
residue.

Add the acid solution containing the tantalum and tungsten to a 100-ml separati
funnel and shake for 2 min with 10 ml of DIPK (or hexone) previously condition
with 0.4 N hydrofluoric acid 12 N sulphuric acid. Remove the aqueous phase a
extract with a further 10 ml of the conditioned organic solvent. Combine the orga
phases and shake briefly with 10 ml of the mixed acid solution. Retain the aque
phase and combine it with the parent solution. The tungsten present is contained
the combined aqueous phases and tantalum in the organic solvent.

Procedure for tungsten

Combine the aqueous phases from the separation in a 150-ml beaker, add 15
of concentrated nitric acid and digest on a hot-plate in a good fume cupboard. Isol
the precipitated tungsten oxide by spinning in a centrifuge, wash the precipitate w
hot concentrated nitric acid and reject the washings. Dissolve the oxide in 0.880
ammonia solution, dilute to 15 ml, spin in a centrifuge and discard the residue, if ar
Digest on a water bath with concentrated nitric acid to precipitate tungsten oxi

the precipitate, dissolve in the minimum volume of 0.880 M ammonia solution,
in a centrifuge and reject any residue. The tungsten oxide–ammonium tungstate
may be repeated and combined with ferric hydroxide scavenges should this be
sary to achieve radiochemical purity.

cipitate tungsten oxinate in boiling, slightly alkaline solution by the slow
ion of 1 ml of 5% 8-hydroxyquinoline solution in 2 N acetic acid. After the
ion of 8-hydroxyquinoline acidify the solution with acetic acid, remove tungsten
te by spinning in a centrifuge, wash with water and finally alcohol and slurry
a weighed counting tray with a little alcohol. Dry under an infra-red heating
, weigh for chemical yield determination and count. Chemical yields are normally
in the range 40–60%.

dure for tantalum

ake the combined DIPK extracts from the separation with 10 ml of 0.4 N
fluoric acid/12 N sulphuric acid solution in a 100-ml separating funnel and
t the aqueous phase. Add 10 ml of 5% hydrogen peroxide solution and shake for
n. Transfer the aqueous phase to a 100-ml beaker, add 1 drop of phenolphthalein
ion followed by 0.880 ammonia until the solution is just pink, dilute to 50 ml
heat on a hot-plate until hydrogen peroxide is destroyed and precipitation of
ated tantalum pentoxide is complete. Isolate the oxide by spinning in a centri-
dissolve in 10 ml of 0.4 N HF/12 N H$_2$SO$_4$ solution and re-extract with condi-
d DIPK rejecting the aqueous phase. Back extract into 5% hydrogen peroxide
ion and precipitate with ammonia as before. Dissolve the hydrated oxide in the
mum volume of 40% hydrofluoric acid (1–2 drops), dilute to 5 ml with deminer-
d water and add 10 drops of 0.1 molar tri-2,2'-dipyridyl ferrous sulphate. Spin
centrifuge to isolate the precipitate, wash with 5 ml of demineralised water and
ly with alcohol. Slurry with a little alcohol onto a tared counting tray, remove
solvent by heating under a lamp, weigh for chemical yield determination and
t. Chemical yields of 40–60% are normal.

here hexone is used instead of DIPK in the separation, back extraction with
ogen peroxide sometimes results in emulsification. The emulsion is readily broken
pinning in a centrifuge.

ulations

unt the samples and standards and correct the measured activities for back-
nd, counter dead-time, and with tungsten, for decay during counting. The
unt of tantalum or tungsten present in the sample X, is given by the relation:

$$\frac{\text{Mass of } X \text{ in sample}}{\text{Mass of } X \text{ in standard}} = \frac{\text{Activity from } X \text{ in sample corrected for 100\% chemical yield}}{\text{Activity from } X \text{ in standard corrected for 100\% chemical yield}}$$

irm the radiochemical purity of the final source by means of half-life deter-
tions (for tungsten), beta absorption curves and gamma spectra.

ACCURACY AND PRECISION

e idea of the precision of the method developed when applied to the deter-
tion of tantalum and tungsten at sub-microgram levels may be obtained from

TABLE V

Sample	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
G1	1.63, 1.54, 1.54, 1.56, 1.57, 1.54, 1.61, 1.74	1.59	0.40, 0.47, 0.41, 0.37, 0.37, 0.36, 0.41	0.40
W1	0.47, 0.48	0.48	0.42, 0.42, 0.41, 0.47	0.43
G1 (Ground by authors)	1.29, 1.37	1.33	0.11, 0.12	0.12

TABLE VI

TANTALUM AND TUNGSTEN CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF E GREENLAND AND OF TWO DUNITES

Sample and origin	Ta content (p.p.m.)	Average (p.p.m.)	W content (p.p.m.)	Average (p.p.m.)
E.G. 3058 transgressive granophyre sill	1.29, 1.33, 1.34	1.32	0.41, 0.45, 0.45, 0.48, 0.50	0.46
E.G. 4332 hedenbergite granophyre	3.33, 3.60, 3.66	3.53	1.02, 1.02, 1.07, 1.14, 1.16, 1.16, 1.17	1.11
E.G. 4329 purple band ferrogabbro	1.35, 1.63	1.49	0.41, 0.43, 0.47	0.44
E.G. 4328 purple band ferrogabbro	1.26, 1.30, 1.36	1.31	0.18, 0.19, 0.20, 0.21	0.20
E.G. 4327 purple band ferrogabbro	0.90, 0.99	0.95	0.31, 0.52	0.42
E.G. 4318 lower ferrogabbro	0.55, 0.62	0.59	0.37, 0.46	0.42
E.G. 5196 hortonolite ferrogabbro	1.52, 1.53, 1.60	1.55	0.08, 0.08, 0.10, 0.10	0.09
E.G. 5181 hortonolite ferrogabbro	0.40, 0.45	0.43	0.12, 0.12	0.12
E.G. 4427 middle gabbro	1.09, 1.14	1.12	0.12, 0.12	0.12
E.G. 5086 hypersthene-olivine gabbro	0.33, 0.43	0.38	0.13, 0.14	0.14
E.G. 4507 chilled marginal gabbro	0.43, 0.45, 0.45, 0.45, 0.46, 0.53	0.46	0.17, 0.19, 0.20, 0.20, 0.20, 0.22, 0.23, 0.23, 0.23, 0.24, 0.24, 0.25	0.22
Dunite A. 301	0.022, 0.027	0.025	0.14, 0.15	0.15
Dunite S. 39	0.010, 0.012	0.011	0.42, 0.48	0.45

TABLE VII

TANTALUM IN STANDARD STEEL SAMPLES

Sample	Published tantalum content (%) [a]	Tantalum content by activation (%)	Average tantalum content by activation (%)
B.C.S. 246 '18/12' Stainless Steel	< 0.02	0.0283, 0.0285	0.028
B.C.S. 271 Mild Steel	0.008	0.0032, 0.0032	0.003
B.C.S. 272 Mild Steel	0.0015	0.0007, 0.0008	0.0008
B.C.S. 273 Mild Steel	0.020	0.0129, 0.0133	0.013
B.C.S. 274 Mild Steel	0.0065	0.0038, 0.0041	0.004
B.C.S. 275 Mild Steel	0.003	0.0025, 0.0031	0.003
N.B.S. 123B Stainless Steel Nb–Ta stabilised	0.20	0.179, 0.189, 0.194 0.205, 0.209, 0.216	0.20

[a] not claimed by manufacturers to be more than approximate except in case of NBS 123B.

TABLE VIII

TUNGSTEN IN STANDARD STEEL SAMPLES

Sample	Published tungsten content (average) (%)	Tungsten content by activation (%)	Average tungsten content by activation (%)
B.C.S. 246 '18/12' Stainless Steel	0.22	0.181, 0.188, 0.182, 0.174, 0.185	0.18
B.C.S. 271 Mild Steel	0.015	0.011, 0.011, 0.014, 0.014	0.013
B.C.S. 272 Mild Steel	< 0.01	0.0013, 0.0013	0.0013
B.C.S. 273 Mild Steel	0.28	0.278, 0.300	0.29
B.C.S. 274 Mild Steel	0.04	0.0299, 0.0321, 0.0358, 0.0363	0.034
B.C.S. 275 Mild Steel	0.05	0.0392, 0.0410, 0.0436, 0.0442	0.042
B.C.S. 276 Mild Steel	0.205	0.208, 0.212	0.21
B.C.S. 277 Mild Steel	0.125	0.122, 0.131	0.13
N.B.S. 123B Stainless steel Nb–Ta stabilised	0.18	0.160, 0.161, 0.161, 0.167	0.16

the results for the analyses of the granite G1 and the diabase W1 recorded in Table
and the results for samples from the Skaergaard Intrusion (Table VI). Attempts
assess the accuracy of the method are hampered by the lack of suitable standar
materials whose trace element content has been unequivocally established. A numb
of commercially available standard steel samples containing low concentrations
tantalum and tungsten are available and were examined (Tables VII and VIII).

It must be emphasised that the published results for the tantalum contents of t
British Chemical Standard steels examined are not claimed by the manufacturers
be anything more than approximate. Only one steel sample (N.B.S. 123B) with
low, accurately known tantalum content was available and with this sample excelle
agreement between the observed and published tantalum contents was obtained. T
agreement between the published and observed tungsten contents of the steel samp
examined was satisfactory.

RESULTS AND DISCUSSION

FAIRBAIRN et al.[26] have proposed a granite G1 from Westerly, Rhode Island, an
a diabase W1 from Centerville, Virginia as international standards for the dete
mination of major and minor constituents of igneous rocks. Uniform samples of G
and W1 supplied pulverised by the U.S. Geological Survey were available and
analysis gave the results listed in Table V. In addition a lump of the parent rock w
available in the case of G1. Pieces totalling approximately 10 g in weight were remov
from the parent rock sample, broken down in a mild steel percussion mortar and ha
picked to exclude any pieces forming a part of the original surfaces. Finally the sam
was further broken down in the percussion mortar before being ground in aga
sampled and analysed. The results for this material are also included in Table V.

In view of the small sample weight taken initially and the subsequent ha
picking, these results are open to objection on the grounds of the possible inhom
geneity of the parent sample. However, the tantalum and especially tungsten conter
obtained in a sample of G1 ground in the authors' laboratory are significantly low
than those from samples ground by the U.S. Geological Survey.

The possibility that the sample may have become contaminated after receipt
the authors' laboratory was considered unlikely in view of the precautions exercis
As soon as the sample was received it was subdivided into a series of clean, d
numbered sample tubes. No significant differences in the tantalum and tungst
contents of G1 were detectable whichever sample tube was used as a source of t
sample. During the course of the work described in this paper a further batch of
was received into the laboratory. Results obtained on the new batch of material w
no different from those obtained with the previous batch.

A series of rock samples from the Skaergaard Intrusion of East Greenland (kin
supplied by Prof. L. R. WAGER, Department of Geology and Mineralogy, Univers
of Oxford) were examined and the results for repeated analyses are included
Table VI. These samples had been ground in the Mineral Dressing Group of
Chemical Engineering Division, Atomic Energy Research Establishment, Harwell,
pulverising in a stainless steel percussion mortar followed by sieving through
100-mesh sieve. A single small piece of E.G. 4507 (chilled marginal gabbro)
available as well as the finely ground material. This was ground and sampled in
authors' laboratories using the apparatus and method described in the preparat

Gɪ. Analyses of duplicate samples gave tantalum contents of 0.34 and 0.34 p.p.m. and tungsten contents of 0.16 and 0.20 p.p.m. Duplicate samples of the material found by the Mineral Dressing Section examined at the same time gave tantalum contents of 0.43 and 0.53 p.p.m. and tungsten contents of 0.22 and 0.25 p.p.m. Because of the small samples used these results are open to objection for the same reason as given in the case of Gɪ.

Also included in Table VI are results for the tantalum and tungsten contents of two ultrabasic rocks (dunites). Sample S. 39 from Balsam Quarry, North Carolina, was kindly supplied by Dr. E. A. VINCENT of the Department of Geology and Mineralogy, University of Oxford.

A number of stony and iron meteorites were examined and their results are recorded in Tables IX and X. All of these samples had been prepared for analysis in the authors' laboratory. Johnstown, Ness County, Long Island and Forest City stony

TABLE IX

TANTALUM AND TUNGSTEN CONTENTS OF SOME STONY METEORITES

Sample and origin	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
Johnstown, Weld Co., Colorado	0.007, 0.009	0.008		
Ness Co., Kansas	0.022, 0.022	0.022		
Long Island – Phillips Co., Kansas	0.027, 0.027	0.027		
Forest City, Winnebago Co., Iowa	0.022, 0.023	0.023		
Chateau Renard	0.024, 0.025, 0.027, 0.030	0.027	0.15, 0.15, 0.17	0.16
Holbrook, Arizona	0.024, 0.026	0.025	0.15, 0.15	0.15
Chandakaphur	0.018, 0.019, 0.020, 0.022	0.020	0.11, 0.12, 0.13	0.12
Bjurböle	0.020, 0.021	0.021	0.07, 0.09	0.08
Tabory (Ochansk)	0.018, 0.018	0.018	0.14, 0.19	0.17

TABLE X

TANTALUM AND TUNGSTEN CONTENTS OF SOME IRON METEORITES

Sample and origin	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
Canyon Diablo	0.0009, 0.001, 0.003, 0.004	0.002	1.42, 1.54, 1.87	1.61
Henbury	0.004, 0.005	0.005	0.75, 0.77	0.76
San Martin	0.0006, 0.0009	0.0008	2.60, 2.68	2.64

meteorite samples were available from earlier work. These samples had been drill
with a tungsten carbide tipped drill and in view of the possibility of tungsten contam
ination during this operation no results for this element have been recorded. T
other stony meteorites examined had been broken down in a mild steel percussi
mortar and ground in a new agate mortar. Iron meteorites were cut into small piec
with a hacksaw, washed with dilute hydrochloric acid and acetone and stored in
airtight bottle. Before sampling for irradiation, iron meteorite samples were given
further surface etch with a dilute hydrochloric acid–hydrogen peroxide solution an
then washed with de-ionised water and finally acetone.

   In view of the precautions exercised in the preparation of meteorite samples, it
considered that significant contamination is unlikely. Results obtained by t
analysis of G1 and E.G. 4507 ground in the authors' laboratory were in all cases low
than results obtained on samples of these materials which were received into t
laboratory already ground. Consequently the tantalum and tungsten contents f
G1 supplied by the U.S. Geological Survey and all the Skaergaard Intrusion sampl
in Table VI must be regarded as accurate in a relative sense only. While these resu
represent the tantalum and tungsten contents of the samples as received, it is possib
that they may not represent the absolute contents of the natural rock samples.

   Clearly the use of G1 as a standard for intercomparison purposes is still valid, an
as pointed out earlier the low values, obtained on small pieces only may well be loc
values and not truly representative. Nevertheless from the evidence, it seems cle
that the greatest care is necessary in the preparation for analysis of geologic
specimens required for trace tungsten and tantalum determinations.

POSSIBLE INTERFERING ELEMENTS

Methods for the production of ^{182}Ta and ^{187}W other than by the (n, γ) reacti
may be postulated. These alternative methods of formation represent potent
sources of error in the determination. Amongst the reactions likely to introdu
errors into the determination may be mentioned the (n, p) and (n, α) reactions broug

TABLE XI

CONFLICTING NUCLEAR PROCESSES IN THE ESTIMATION OF TANTALUM AND TUNGSTEN BY $(n,$
REACTION

Parent isotope	Abundance (%)	Reaction	Product
$^{182}_{74}$W	26.5	(n, p)	$^{182}_{73}$Ta
$^{185}_{75}$Re	37.1	(n, α)	$^{182}_{73}$Ta
$^{183}_{74}$W	14.3	(γ, p)	$^{182}_{73}$Ta
$^{187}_{75}$Re	62.9	(n, p)	$^{187}_{74}$W
$^{190}_{76}$Os	26.4	(n, α)	$^{187}_{74}$W

ut by the more energetic component of the neutron flux and the (γ, p) reaction
uced by the pile gamma flux.

ome of the more important reactions (other than the (n, γ)) which can lead to the
duction of ^{182}Ta and ^{187}W are listed in Table XI. The elemental abundances of
gsten, rhenium and osmium are low and unless the reactions enumerated have
eptionally high cross-sections, interference at any significant level is unlikely to be
ous. An upper limit to the radioactivity produced by the conflicting nuclear reac-
is listed in Table XI may be determined by irradiating pure samples of tungsten,
ium and osmium or their compounds and determining the ^{182}Ta and ^{187}W
vities present in them (Table XII). Any tantalum or tungsten present as impuri-
in the samples examined in Table XII will contribute by (n, γ) reaction to the
vity produced, and in consequence the results included in the table are to be
arded as a maximum.

TABLE XII

ARENT TANTALUM CONTENT OF TUNGSTEN AND RHENIUM AND THE APPARENT TUNGSTEN
CONTENT OF RHENIUM AND OSMIUM

Element	Apparent tantalum content (average) (p.p.m.)	Apparent tungsten content (average) (p.p.m.)
Tungsten	0.23	—
Rhenium	4.4	3.54
Osmium	—	1.32

The value of the upper limit of interference caused by conflicting nuclear processes
tungsten, rhenium and osmium determined above, coupled with a knowledge of
approximate contents of these elements likely to be encountered in any of the
mples analysed, suggests that errors produced by them are insignificant and can
ignored.

CONCLUSION

e method whose development and application has been described in this paper
s been applied to the determination of tantalum at levels down to $8 \cdot 10^{-10}$ g and
gsten down to $2 \cdot 10^{-9}$ g. These results represent the maximum sensitivity obtain-
e for tantalum with the short irradiation periods used: the tungsten sensitivity
ld have been extended if necessary. Longer irradiations with the existing facility
uld enable the sensitivity to be improved and there is every indication that the
sitivities quoted in the section on nuclear data could be attained. No radio-
mical impurity has been detected in any of the final sources from the variety of
mples examined.

SUMMARY

method for the determination of sub-microgram amounts of tantalum and tungsten in rocks
meteorites by neutron activation analysis is described. Radiochemical separation from the
ponents of the irradiated sample was employed to provide sources for measuring ^{182}Ta and
W by beta and gamma counting and by gamma spectrometry. Determinations of tantalum
he lower limit of $8 \cdot 10^{-10}$ g and tungsten at $2 \cdot 10^{-9}$ g have been made. Amongst the materials
mined using the method were the intercomparison rocks G1 and W1, rock samples from the

Skaergaard Intrusion of East Greenland and a number of iron and stony meteorites. In additi
a number of standard steel samples of known tungsten content and one of known tantalum conte
were examined and good agreement was observed between the published results and those det
mined by activation analysis.

RÉSUMÉ

Une méthode est proposée pour l'ultramicrodosage du tantale et du tungstène dans les roc
et les météorites par activation au moyen de neutrons. Une séparation radiochimique d'avec
composants de l'échantillon irradié a été effectuée en vue de la mesure du ^{182}Ta et du ^{187}W p
comptage beta et gamma et par spectrométrie gamma.

ZUSAMMENFASSUNG

Ultramikromengen von Tantal und Wolfram in Gesteinen und Meteoriten können durch Ak
vierung mit Neutronen bestimmt werden. Zur Messung von ^{182}Ta und ^{187}W durch Beta u
Gamma-Zählung und Gamma-Spektrometrie wurden die Komponenten der bestrahlten Pro
nach radiochemischen Methoden abgetrennt.

REFERENCES

[1] K. RANKAMA, *Bull. comm. géol. Finlande*, (133) 1954.
[2] E. B. SANDELL, *Am. J. Sci.*, 244 (1946) 643.
[3] A. P. VINOGRADOV, E. E. VAINSHTEIN AND L. J. PAVLENKO, *Geochemistry*, No. 5 (1958) 4
[4] E. N. JENKINS AND A. A. SMALES, *Quart. Revs.*, 10 (1956) 83.
[5] D. H. F. ATKINS AND A. A. SMALES, *Advances in Inorganic Chemistry and Radiochemist*
   Vol. 1, Academic Press, New York 1959, p. 315.
[6] M. CABELL AND A. A. SMALES, *Analyst*, 82 (1957) 390.
[7] A. KOHN, *Compt. rend.*, 236 (1953) 1419.
[8] J. V. P. LONG, *Analyst*, 76 (1951) 644.
[9] J. BEYDON AND C. FISHER, *Anal. Chim. Acta*, 8 (1953) 538.
[10] G. G. EICHOLZ, *Nucleonics*, 10 (12) (1952) 58.
[11] G. W. C. MILNER AND A. A. SMALES, *Analyst*, 79 (1954) 425.
[12] W. A. BROOKSBANK, G. W. LEDDICOTTE AND S. A. REYNOLDS, *Anal. Chem.*, 28 (1956) 10
[13] J. A. JAMES AND D. H. RICHARDS, *J. Electronics and Control*, 3 (1957) 500.
[14] M. HUARINGA, *Nature*, 177 (1956) 85.
[15] G. LELIAERT, J. HOSTE AND Z. EECKHOUT, *Nature*, 182 (1958) 600.
[16] G. LELIAERT, J. HOSTE AND Z. EECKHOUT, *Talanta*, 2 (1959) 115.
[17] A. A. SMALES AND B. A. LOVERIDGE, *Anal. Chim. Acta*, 13 (1955) 566.
[18] D. J. HUGHES AND J. A. HARVEY, *U. S. Atomic Energy Comm. Report* No. BNL 325, 1955
[19] F. T. SEELYE AND T. A. RAFTER, *Nature*, 165 (1950) 317.
[20] J. KLEINBERG, *U. S. Atomic Energy Comm. Report* No. LA-1721, 2nd Ed., 1958.
[21] W. W. MEINKE, *U. S. Atomic Energy Comm. Report* No. AECD-2738, 1949.
[22] P. C. STEVENSON AND H. G. HICKS, *Anal. Chem.*, 25 (1953) 1517.
[23] G. R. WATERBURY AND C. E. BRICKER, *Anal. Chem.*, 29 (1957) 1474.
[24] N. S. POLNETKOV AND V. A. NAZERENKO, *J. Appl. Chem. (U.S.S.R.)*, 11 (1938) 1028.
[25] J. GILLIS, Z. EECKHOUT AND K. PONA, *Verhandel. Koninkl. Vlaam. Acad. Wetenschap. Be*
   6 (10) (1944) 5.
[26] H. W. FAIRBAIRN *et al.*, *Bull. U.S. Geol. Survey*, No 980 (1951) 1.

ECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

SHOZO SHIBATA

Government Industrial Research Institute, Nagoya (Japan)

INTRODUCTION

merous colorimetric reagents have been proposed for uranium determinations. enzoylmethane[1], 2-acetoacetylmethane[2], neothorin[3] (arseneazo) offer high sitivity, but can be applied only to solutions from which interfering ions have n removed. CHENG AND BRAY[5] recently reported a new, sensitive reagent for nium, 1-(2-pyridylazo)-2-naphthol (PAN), which reacts with many heavy met-[4-9]. CHENG[7] states that in an alkaline solution containing strong complexing nts, only uranium precipitates when PAN is added. The precipitated uranium s extracted into dichlorobenzene, and the uranium determined spectrophotometric-y at 570 mμ. However, he stated that this precipitate is not soluble in chloroform carbon tetrachloride, hence uranium–PAN complex could not be extracted with oroform or carbon tetrachloride. The results described below show that the uranyl mplex in ammoniacal medium is not completely soluble in chloroform; but in the esence of sodium chloride or sodium sulfate, it can be easily extracted by chloroform.

paratus and reagents

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, with 1-cm cells. Beckman H-2 type pH meter was used.

Standard solution of uranium: This was prepared by dissolving 1.200 g of uranyl nitrate hexa-drate in 1 l of distilled water. It was standardized by the oxine method.

Ethylenediaminetetraacetic acid (disodium salt) (EDTA) solution: A 0.1 M aqueous solution was pared from the reagent grade EDTA.

1-(2-pyridylazo)-2-naphthol solution (PAN): A 0.1% solution was prepared by dissolving 100 mg PAN (Tokyo Kasei Chem. Co.) in absolute methanol, filtering through glass wool, and diluting 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution (pH 9.5–10.0): Ammonium chloride–ammonia mixed solution was used for the adjustment.

All other chemicals used in this work were pure Wako's reagents.

ocedure

An aliquot of the slightly acid or neutral solution containing 2 to 100 μg of uranium s mixed with 5 ml of the buffer solution, 2 ml of 0.1 M EDTA solution and 2.0 g sodium chloride, and diluted to approximately 20 ml; the pH was adjusted to –10 with ammonium hydroxide, if necessary. 2 ml of 0.1% PAN was added and owed to stand for five min. Exactly 10 ml of chloroform was added to the mixture ich was then shaken vigorously for 1 to 2 min. The chloroform extract was cen-fuged and the absorbance measured at 560 mμ against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the PAN reagent in chloroform and of the chelate formed with uranium are presented in Fig. 1. These curves were obtained with the addition of 2 ml of 0.1 M EDTA to complex interfering metals, such as copper and zinc. The maximum absorption of the red uranium dye chelates appears at approximately 560 mμ, where the dye itself does not absorb appreciably.
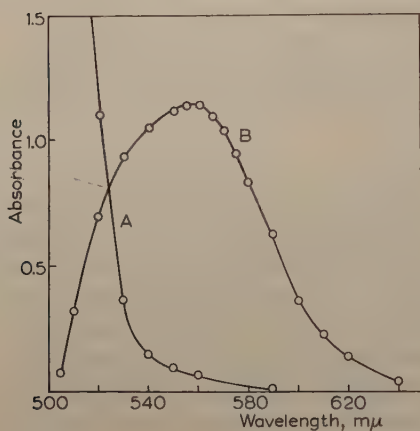

Fig. 1. Absorption spectra of uranium–PAN complex in chloroform. A, uranium(VI)–PAN complex, 12.8 μg U/ml. B, PAN.
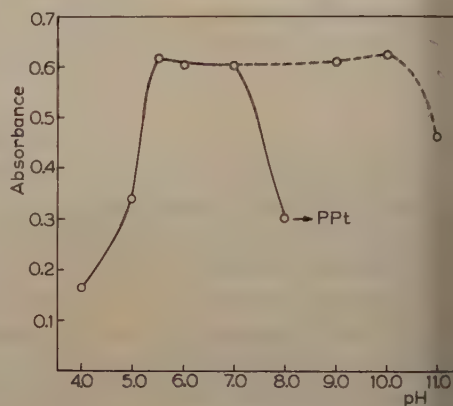
Fig. 2. Effect of pH on absorbance of chloroform extract ——— no sodium chloride ---- sodium chloride added ($\lambda = 560$ mμ

Beer's law

The absorbances of uranium–PAN solution were found to be linearly related to the concentration of uranium. Typical data for a calibration curve are given in Table

TABLE I

CALIBRATION DATA FOR COLORIMETRIC URANIUM ANALYSES

Uranium concn., p.p.m.	Absorbance at 560 mμ
1.15	0.102
2.30	0.202
4.60	0.408
5.75	0.511
6.90	0.615
8.05	0.718
9.20	0.820

Effect of pH

A series of solutions containing definite amounts of uranyl solution and 1 ml of 0.1 PAN was prepared. Ammonium chloride–ammonium hydroxide or acetic acid sodium acetate was used for the pH adjustment. Fig. 2 shows that the optimum p range was from pH 5.5 to 10.0. Below pH 4.0 no significant complex between uraniu

PAN was formed. At higher pH (above *ca.* 8.0), the complex formed between
nium and dye could not be extracted completely by chloroform (unless sodium
ride was added) or by carbon tetrachloride.

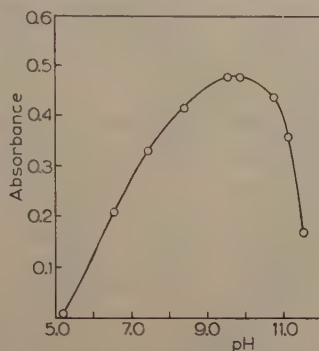3. Effect of pH on absorbance of chloroform extract in the presence of EDTA. Sodium chloride
added. ($\lambda = 560$ mμ)

A second series of solutions containing definite amounts of uranyl nitrate solution,
ml of 0.1 M EDTA solution, 2 g of sodium chloride and 2 ml of 0.1% dye solution
s prepared. The results are given in Fig. 3. Uranium–PAN complex could be
tracted very smoothly by chloroform in the presence of sodium chloride but the
timum pH range was rather narrow (pH 9.5–10). Below pH 6 or above pH 12, no
nificant complex between uranium and PAN was formed. Because the pH is such
critical factor in obtaining the maximum color development and reproducible
ults, the pH of the solution should be carefully adjusted to ±0.2 unit, in addition
using a buffer solution.

fect of complexing agents

Several ml of 0.1% cyanide solution and about 0.1 g of sodium fluoride did not show
y effect, but EDTA affected the color development to some degree. EDTA and
AN competed for the uranium when large amounts of free EDTA were present.
only a slight excess of EDTA was present, such competition was overcome by
ding more dye. Though uranyl ion forms a stronger complex with PAN than with
DTA, more dye should be added when more EDTA is present. Two or three ml of
1% dye solution was satisfactory when 0.5 mmoles of EDTA was present. The
nounts of complexing agent added for masking purposes should be slightly in
cess. Cyanide is very effective in eliminating interference from copper, nickel and
ercury.

TABLE II

EFFECT OF VARIOUS ADDITIONAL SALTS

Salts	g	Absorbance at 560 mμ
NaCl	2.5	0.572
Na$_2$SO$_4$	2.5	0.574
KNO$_3$	2.5	0.490
KCN	1.0	0.272

Effect of various additional salts on absorbance

Table II shows the effect of various additional salts, and Table III shows the effect of varying the amount of sodium chloride. Sodium chloride or sodium-sulfate is the most suitable additional salt; that 1 g of sodium chloride is sufficient to complete the extraction of the uranium–PAN chelate by chloroform.

TABLE III

EFFECT OF AMOUNTS OF SODIUM CHLORIDE

NaCl added g	Absorbance at 560 mμ
1.0	0.574
1.5	0.576
2.0	0.584
2.5	0.572
3.0	0.574

Time of standing

Table IV shows that the minimum time for standing before extraction with chloroform for complete color development of the uranium–PAN complex was five min. After this time the color was very stable and suitable for quantitative work.

TABLE IV

TIME OF STANDING

Time min	Absorbance at 560 mμ
1	0.495
3	0.493
5	0.490
10	0.490

Reproducibility and accuracy

The reproducibility of the method was tested by determining the recovery of 2.0, 5.5, and 9.0 p.p.m. of uranium on 11 successive samples. The results are given in Table V. The standard deviation was calculated using the formula:

$$\text{S. D. } \alpha = \sqrt{\frac{(\overline{X} - X)^2}{N - 1}}$$

where $(\overline{X} - X)$ is the deviation of each determination from the average, and N is the total number of determinations.

Interfering ions

To study the effect of various metals on this determination of uranium, a solution containing both uranium and the metal was treated according to the procedure. The results obtained are given in Table VI and VII. The data show that uranium could be determined in the presence of many heavy metals which frequently interfere with other colorimetric methods for uranium.

Chloride, bromide, iodide, sulfate, nitrate, carbonate, acetate and fluoride did not interfere. Phosphate interfered with the color reaction because uranyl phosphate was precipitated.

TABLE V
REPRODUCIBILITY OF THREE CONCENTRATIONS

'o.	2.0 p.p.m. U		5.5 p.p.m. U		9.0 p.p.m. U	
	Absorbance vs. blank	Dev. from mean absorbance	Absorbance vs. blank	Dev. from mean absorbance	Absorbance vs. blank	Dev. from mean absorbance
1	0.179	0.001	0.485	0.003	0.790	0.014
2	0.177	0.003	0.480	0.008	0.800	0.004
3	0.180	0.000	0.490	0.002	0.810	0.006
4	0.177	0.003	0.490	0.002	0.795	0.009
5	0.180	0.000	0.489	0.001	0.815	0.011
6	0.178	0.002	0.491	0.003	0.800	0.004
7	0.181	0.001	0.492	0.004	0.810	0.006
8	0.179	0.001	0.487	0.001	0.805	0.001
9	0.183	0.003	0.490	0.002	0.800	0.004
10	0.179	0.001	0.491	0.003	0.810	0.006
11	0.183	0.003	0.482	0.006	0.805	0.001
Range	0.006		0.009		0.025	
Median	0.180		0.487		0.802	
Mean $\overline{X}$	0.180		0.488		0.804	
Av. Dev.	0.0016		0.0032		0.0060	
S. D. α	0.0021		0.0040		0.0075	
% Dev.	1.17		0.82		0.93	

$$\% \text{ Dev.} = 100\alpha/\overline{X}$$

'urther work on the applicability of PAN to the determination of small amounts
ranium in ores and alloys is now in progress.

TABLE VI
DETERMINATION OF URANIUM IN THE PRESENCE OF THORIUM
(59.0 µg uranium taken)

Th added mg	Uranium µg	
	Found	Error
0.22	59.3	+0.3
0.44	59.7	+0.7
0.66	60.0	+1.0
1.10	61.2	+2.2
2.20	61.3	+2.3

TABLE VII
EFFECT OF METALS ON DETERMINATION OF URANIUM WITH PAN
(59.0 µg uranium taken)

Metal added	Amt. added mg	Added as	Complexing agents	Uranium µg	
				Found	Error
Ag	1.0	AgNO$_3$	KCN	57.5	— 1.5
As	1.0	K$_3$AsO$_3$	EDTA	59.0	± 0.0
Al	1.0	AlCl$_3$	EDTA	59.1	+ 0.1
Al	5.0	AlCl$_3$	EDTA	65.7	+ 6.7
Bi	0.5	Bi(NO$_3$)$_3 \cdot$ 5H$_2$O	EDTA	61.8	+ 2.8
Ce	1.2	Ce(NO$_3$)$_3 \cdot$ 6H$_2$O	EDTA	59.0	± 0.0
Cd	1.0	Cd(NO$_3$)$_2 \cdot$ 4H$_2$O	EDTA	59.7	+ 0.7
Ca	6.0	CaCl$_2$	EDTA	59.5	+ 0.5
Cu	1.0	CuSO$_4 \cdot$ 5H$_2$O	EDTA	57.7	— 1.3
Fe	1.1	FeCl$_3$	EDTA	59.3	+ 0.3
Ga	0.6	GaCl$_3$	EDTA	59.0	± 0.0

Continued

TABLE VII (continued)

Metal added	Amt. added mg	Added as	Complexing agents	Uranium μg	
				Found	Error
Hg	1.0	$HgCl_2$	KCN	59.0	± 0.0
Mn	1.0	$MnSO_4 \cdot 4H_2O$	EDTA	57.1	— 1.9
Mo	1.1	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	EDTA	58.0	— 1.0
Ni	1.0	$NiSO_4 \cdot 7H_2O$	KCN	59.2	+ 0.2
Zr	0.5	$Zr(SO_4)_2 \cdot 4H_2O$	EDTA+KCN	57.0	— 2.0
Zn	1.0	$ZnSO_4 \cdot 7H_2O$	EDTA	59.2	+ 0.2
Pb	1.0	$Pb(NO_3)_2$	EDTA	59.0	± 0.0
Mg	5.0	$MgCl_2$	EDTA	60.2	+ 1.2
La	0.6	$La(NO_3)_3 \cdot 6H_2O$	EDTA	62.0	+ 3.0
In	0.5	$InCl_3$	EDTA	60.5	+ 1.5
Sn	1.0	$SnCl_4$	EDTA	70.1	+11.1
Ti	0.5	$Ti(SO_4)_2$	EDTA+NaF	63.3	+ 4.3
V	1.3	$Na_3VO_4 \cdot 10H_2O$	EDTA	59.0	± 0.0
W	1.0	$Na_2WO_4 \cdot 2H_2O$	EDTA	57.5	— 1.5

ACKNOWLEDGEMENTS

SUMMARY

1-(2-Pyridylazo)-2-naphthol (PAN) reacts with uranium to form a deep red precipitate in ammor acal solutions; this can be extracted with chloroform if sodium chloride or sulfate is added and has a maximum absorption at 560 mμ. The color is stable and follows Beer's law. Trace amoun of uranium may be determined in the presence of many metals without prior separation if stror complexing agents, such as EDTA or cyanide, are added.

RÉSUMÉ

De nombreux cations réagissent avec l'(α-pyridylazo)-1-hydroxy-2-naphtalène; cependant, présence d'agents complexants, tels que l'acide éthylènediaminotétracétique et le cyanure, se l'uranium donne un précipité rouge foncé pouvant être extrait par le chloroforme, en présence chlorure ou de sulfate de sodium.

ZUSAMMENFASSUNG

Uran bildet mit 1-(2-Pyridylazo)-2-naphthol (PAN) in Gegenwart von Komplexbildnern (EDT Cyaniden) einen rot gefärbten Niederschlag, der in Gegenwart von Natriumchlorid oder Natriu sulfat mit Chloroform extrahiert werden kann.

REFERENCES

1 J. H. Yoe, F. Will III, and R. A. Black, Anal. Chem., 25 (1953) 1200.
2 T. Hara, J. Chem. Soc. Japan, Pure Chem. Sect., 78 (1957) 331.
3 S. Shibata and T. Matsumae, Bull. Chem. Soc. Japan, 32 (1959) 279.
4 G. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry, John Wiley & Sor New York 1957, p. 172.
5 K. L. Cheng and R. H. Bray, Anal. Chem., 27 (1955) 782.
6 A. I. Busev and L. V. Kisseleva, Vestnik Moskov. Univ., 4 (1958) 179.
7 K. L. Cheng, Anal. Chem., 30 (1958) 1027.
8 H. H. Gill, R. F. Rolf and G. W. Armstrong, Anal. Chem., 30 (1958) 1788.
9 G. Goldstein, D. L. Manning and O. Menis, Anal. Chem., 31 (1959) 192.

A HETEROMETRIC STUDY OF THE PHENANTHROLINE
MPOUNDS WITH PLATINUM, PALLADIUM AND GOLD HALIDES
AND THEIR ANALYTICAL APPLICATION

MORDECHAI (MAX) BOBTELSKY AND MAURICE MOSCHE COHEN

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem (Israel)

INTRODUCTION

o-Phenanthroline is known analytically because it forms a complex with
n(II), which is very stable and is used for the spectrophotometric determination
ron. Phenanthroline is also used in the gravimetric determination of palladium
l in its separation from platinum[1]. Palladium is precipitated as $PdC_{12}H_8N_2Cl_2$
m hydrochloric acid solution, dried at 110° and weighed. According to RYAN[1],
compound is pale-yellow in colour, very stable, and insoluble in water and most
er solvents. Under similar conditions, RYAN found that the gold compound was
ompletely precipitated. An attempt to separate palladium from gold by the same
cedure was also unsuccessful. DUVAL[1], who studied the chloride compounds of
enanthroline thermogravimetrically, found a temperature limit of 50–389° and
ded "that the formula of the precipitate changes according to the anion associated
h the palladium _before_ precipitation". Up till now very little seems to be known
ut the behaviour and composition of the gold or platinum compounds of phenan-
oline.

This investigation was carried out with a double purpose: firstly, to study the
ctions between phenanthroline and noble metal halides heterometrically, and
ondly, to see if the heterometric method can be used for the determination of
tinum, palladium or gold, singly or in mixtures, with phenanthroline. From
vious studies of the reactions between the noble metal chlorides and nitron, we
ew that insoluble compounds of definite composition were only obtained in the
sence of excess of thiocyanate. Surprisingly, many compounds were quantitatively
ained from the critical points of the different heterometric curves.

t would be impossible to discuss here in detail the structures of the many inter-
diate compounds cited in the tables; attention will be given mainly to the final
↓↓) compounds derived from the titration curves. Their structural presentation
ms to be complex, and may depend on the working conditions.

t different compositions of the analysed solutions, six different _final_ compounds
re obtained at the first maximum optical density points of the curves. Each of
se compounds could be used with almost equal success for the determination of
metals. The error obtained was 1% or less. A parallel study was carried out with
paverine, which contains only one nitrogen atom in the closed rings. The reactions
he noble metals with papaverine were about four times as sensitive as those with

phenanthroline. In almost all cases, one final compound, MePv₂, was obtained wi[th] papaverine. The many compounds obtained with phenanthroline could hardly [be] traced and studied except by heterometry. Apparently the complexes which we[re] formed in the "solid" state were much more varied and interesting than those trace[d] in the homogeneous medium.

EXPERIMENTAL

Reagents

1,10-Phenanthroline (B.D.H. AnalaR) $C_{12}H_8N_2 \cdot H_2O$, was dissolved in water to give a 0.01 [M] stock solution.

Platinum chloride (Johnson, Matthey & Co. Ltd.) ($H_2PtCl_6 \cdot xH_2O$), about 40% platinum. [1 g] was dissolved in 250 ml water (approx. 0.008 M).

Palladium chloride (Johnson, Matthey & Co. Ltd.) 1 g was dissolved in 250 ml 0.2 N HCl (appro[x.] 0.022 M PdCl₂/0.2 N HCl).

Gold chloride (brown) (B.D.H. Laboratory reagent) 1 g of HAuCl₄·3H₂O and 25 ml of N H[Cl] were dissolved in 250 ml of aqueous solution (approx. 0.01 M HAuCl₄/0.1 N HCl).

Technique

The same apparatus and technique were used as in previous investigations[2]. The reacti[on] temperature was always 20°.

RESULTS

1. *Reactions with chloroplatinic acid*

Table I presents titrations carried out at pH values of *ca.* 1 and *ca.* 7 in solutio[n] of chloride or thiocyanate with phenanthroline (P) as titrant. The table also contai[ns]
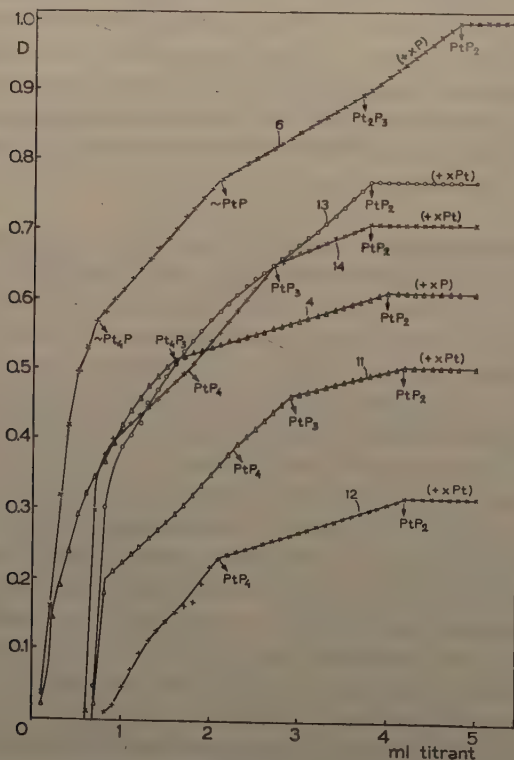

Fig. 1. Titrations of chloroplatinic acid solutions with phenanthroline and the reverse.

a few reverse titrations. The course of some of these experiments is presented in Fig. 1 (the same enumeration is used in the tables and in the corresponding curves). In all cases, if no precipitation occurred in the direct titration, the same held true for the reverse titration. In the presence of chloride no precipitation of the metal with phenanthroline occurred at either of the above pH (Expts. 1–2 and 7–8). In the presence of thiocyanate precipitation occurred only at pH *ca.* 1. Only one final compound was always obtained in thiocyanate solutions, *i.e.* $Pt_1P_2 \downarrow\downarrow$. With phenanthroline as titrant (Expts. 3, 4 and 6), theoretical values were obtained at the end-point which was derived from the intersection of the last part of the titration curve with the horizontal maximum density line. The maximum optical density seemed to decrease if too much thiocyanate was present (Expts. 3–4 and 11–12), although the same compound was always quantitatively obtained. A series of inter-mediate compounds were also obtained; these varied according to the direction of the titration. When phenanthroline was titrated with platinum solution, the following intermediates were obtained:

$$Pt_1P_4\downarrow \xrightarrow{+\ Pt} Pt_1P_3\downarrow \xrightarrow{+\ Pt} PtP_2\downarrow\downarrow$$

This indicates that as many as four phenanthroline molecules can somehow be bound to one atom of platinum. In spite of this, the final compound always showed the same empirical composition, namely $Pt_1P_2 \downarrow\downarrow$. The sensitivity of the reaction with platinum was low, so that about 4 mg of platinum were necessary for a titration. The titration time was always 20–30 min, *i.e.* about 2–3 times more than for a corresponding titration of the metal-thiocyanate solution with nitron. The extended time may be
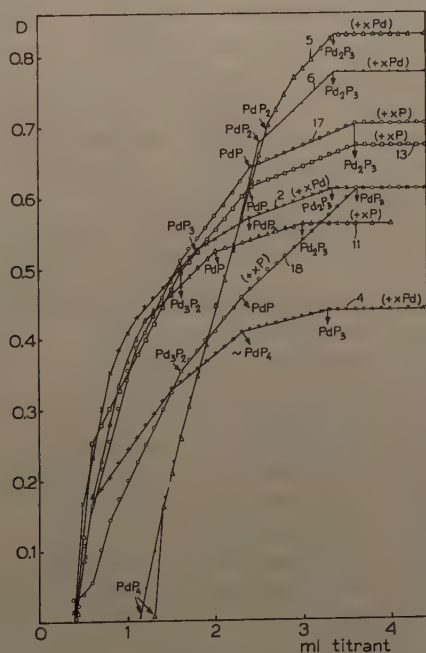

Fig. 2. Titrations of palladium chloride solutions with phenanthroline and the reverse.

TABLE I   General composition: a ml reagen

Expt. No.	Solution titrated	Titrant		Titration time in min
		Name	Molarity	
1	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
2	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.01	
3	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	21
4	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 2 M KCNS	Phenanthr.	0.01	21
5	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
6	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	26
7	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate	Phenanthr.	0.01	
8	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.01	
9	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 0.5 M KCNS	Phenanthr.	0.01	
10	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 2 M KCNS	Phenanthr.	0.01	
11	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.006	20
12	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.006	30
13	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.008	19
14	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.008	18

P = phenanthroline; h = horizontal max. density line; i = intersection point; c = contact point.

TABLE II   General composition: a ml reager

Expt. No.	Solution titrated	Titrant		Titratio time in min
		Name	Molarity	
1	4 ml 0.005 M phenanthr. + 1 ml M HNO_3	$PdCl_2$	0.004	25
2	4 ml 0.005 M phenanthr. + 1 ml M HNO_3 + 2 ml M NaCl	$PdCl_2$	0.004	36
3	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	38
4	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	$PdCl_2$	0.004	35
5	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate	$PdCl_2$	0.004	30
6	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M NaCl	$PdCl_2$	0.004	36
7	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	30
8	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M KCNS	$PdCl_2$	0.004	35
9	3 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	25
10	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	33
11	5 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	32
12	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	35
13	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.005	32
14	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	Phenanthr.	0.005	38
15	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M KCNS	Phenanthr.	0.01	34
16	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate	Phenanthr.	0.005	30
17	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.005	32
18	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	Phenanthr.	0.005	28
19	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M KCNS	Phenanthr.	0.005	32

P = phenanthroline; h = horizontal max. density; c = contact point; i = intersection point; x

10 — a) ml H₂O + x ml titrant.   T = 20°   TABLE I

init. ppt. at (=↑)	Intermediate intersection points (=↓)	End-point (=↓↓)	Calculated molar ratios [Pt] : [P]	Max. density value	% Error
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.2	c. 1.45; i 2.55	i 4.00 h	4:3↓ → 4:5↓ → 1:2↓↓	0.95	0.0
0.1	0.5 ; c 1.6	i 4.00 h	4:3↓ → 1:2↓↓	0.61	0.0
	no ppt.	> 5.0			
0.1	c 0.65; i 2.1; i 3.6	4.80	<4:1↓ → 1:1↓ → 2:3↓ → 1:2↓↓	0.99	0.0
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.7	i 2.25; i 2.9	i 4.20 h	1:4↓ → 1:3↓ → 1:2↓↓	0.51	0.8
0.8	~ i 2.0	i 4.20 h	1:4↓ → 1:2↓↓	0.32	0.8
0.7		i 3.80 h	1:2↓↓	0.77	1.3
0.6	1.8; c 2.7	i 3.80 h	1:4↓ → ~ 1:3↓ → 1:2↓↓	0.71	1.3

(10 — a) ml H₂O + x ml titrant.   T = 20°   TABLE II

init. ppt. int (=↑)	Intermediate intersection points (=↓)	End-point (=↓↓)	Calculated molar ratios [Pd] : [P]	Max. density value	% Error
0.3	c 1.0; 1.7; 2.5	i 3.30 h	1:5↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.63	1.2
0.4	c 1.1; 1.8; 2.4	i 3.35 h	1:4↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.61	0.3
0.4	i 2.4	i 3.30 h	1:4↓ → 1:3↓↓	x 0.54	1.2
0.3	1.5; 2.3	i 3.30 h	1:4↓ ↔ 1:3↓↓	x 0.44	1.2
1.3	2.55; 2.9	i 3.35 h	1:4↑ → 1:2↓ → 3:5↓ → 2:3↓↓	0.82	0.3
1.2	2.5	i 3.35 h	1:4↑ → 1:2↓ → 2:3↓↓	0.77	0.3
0.1	c 1.1	i 3.30 h	~1:5↓ → 2:3↓↓	x 0.79	1.2
0.1	1.0; 1.7	i 3.30 h	1:4↓ → 1:3↓ → 2:3↓↓	x 0.46	1.2
0.5		i 1.8 h	2:3↓↓	0.47	
0.5	0.9; 1.45	i 2.40 h	2:1↓ → 1:1↓ → 2:3↓↓	0.45	0.0
0.4	1.2; 2.00	i 3.00 h	~2:1↓ → 1:1↓ → 2:3↓↓	0.56	0.0
0.4	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.68	0.0
0.4	1.6; 2.40	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.67	0.0
0.6	1.3	i 4.85 h	1:3↓↓	x 0.44	1.0
0.5	(2.0); 2.60	i 3.60 h	~ 1:2↓ → 1:3↓↓	x 0.42	0.0
0.3	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.72	0.0
0.4	(1.1); (1.6); 2.4	i 3.60 h	~2:1↓ → 3:2↓ → 1:1↓ → 2:3↓↓	0.70	0.0
0.4	1.6; 2.30	i 3.62 h	3:2↓ → 1:1↓ → 2:3↓↓	x 0.61	0.6
0.3	2.5	i 3.60 h	1:1↓ → 2:3↓↓	x 0.70	0.0

ange Corning filter No. 3484.

explained by the formation of phenanthroline metal-thiocyanate co-ordinated compounds rather than by a normal cation–anion reaction.

2. *Reactions with palladium chloride*

Table II presents a series of titrations of palladium halide solutions with phenanthroline, and *vice versa* at pH values of *ca.* 1 and *ca.* 7. The course of some titrations is presented in Fig. 2. In all cases precipitation occurred. Final compounds of strictly stoichiometric compositions were always obtained at the first maximum density points, after which a horizontal maximum line was obtained. Either the palladium or the phenanthroline could be determined from these points; the error was generally 0–1 %. The titrations in thiocyanate solutions were carried out with an orange filter. Apparently the same final compound was obtained in all titrations with chloride ($Pd_2P_3 \downarrow\downarrow$). At *ca.* pH 7 in the presence of excess thiocyanate, a similar compound was obtained (Expts. 16–19). This applies also to the intermediate compounds obtained. On the other hand, if the titrations were carried out at *ca.* pH 1

TABLE III   General composition: *a* ml reage

Expt. No.	Solution titrated	Titrant		Titrati time min
		Name	*Molarity*	
1	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$	AuCl$_3$	0.005	25
2	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$	AuCl$_3$	0.005	25
3	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$ + 2 ml *M* NaCl	AuCl$_3$	0.005	22
4	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$ + 1 ml 0.5 *M* NaCl	AuCl$_3$	0.005	25
5	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$ + 2 ml 0.25 *M* KCNS	AuCl$_3$	0.005	19
6	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$ + 2 ml 0.25 *M* KCNS	AuCl$_3$	0.005	20
7	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO$_3$ + 2 ml *M* KCNS	AuCl$_3$	0.005	25
8	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl$_3$	0.005	24
9	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl$_3$	0.005	16
9a	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl$_3$	0.005	24
10	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* NaCl	AuCl$_3$	0.005	25
11	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	AuCl$_3$	0.005	17
12	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	AuCl$_3$	0.005	18
13	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* KCNS	AuCl$_3$	0.005	18
14	4 ml 0.005 *M* AuCl$_3$ + 1 ml 0.5 *M* HNO$_3$	Phenanthr.	0.005	20
15	4 ml 0.005 *M* AuCl$_3$ + 1 ml 0.5 *M* HNO$_3$ + 2 ml *M* NaCl	Phenanthr.	0.005	23
16	5 ml 0.005 *M* AuCl$_3$ + 1 ml 0.5 *M* HNO$_3$ + 2 ml 0.25 *M* KCNS	Phenanthr.	0.005	20
17	5 ml 0.005 *M* AuCl$_3$ + 1 ml 0.5 *M* HNO$_3$ + 2 ml *M* KCNS	Phenanthr.	0.005	26
18	4 ml 0.005 *M* AuCl$_3$ + 1 ml *M* Na-acetate	Phenanthr.	0.005	20
19	4 ml 0.005 *M* AuCl$_3$ + 1 ml *M* Na-acetate + 2 ml *M* NaCl	Phenanthr.	0.005	21
20	4 ml 0.005 *M* AuCl$_3$ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	21
21	4 ml 0.005 *M* AuCl$_3$ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	20

P = phenanthroline; i = intersection point; h = horizontal max. density line; l.i. = linear increase a

in the presence of potassium thiocyanate, the composition of the final compound was $Pd_1P_3 \downarrow\downarrow$ instead of $Pd_2P_3 \downarrow\downarrow$.

For these determinations, approximately one mg of palladium was necessary. The titration time was extended to 30–40 min, *i.e.* about 3–4 times longer than with nitron. (Extended titration times were also observed in similar reactions with papaverine). Again time was needed for the formation of the phenanthroline–palladium complex at room temperature. From the analytical aspect, the use of thiocyanate for chloride had no advantage. There was little difference in the results whether a coloured filter was used or not.

3. *Reactions with gold chloride*

Table III presents a selection of experiments of titrations of gold chloride solutions with phenanthroline and *vice versa* (see also Fig. 3). The reaction with gold has approximately the same sensitivity as that of platinum. Both the chloride and the thiocyanate solutions were tested. The empirical compositions of the final compounds

$\flat$ — a) ml H_2O + x ml titrant.   T = 20°   **TABLE III**

ppt. (=↑)	ml titrant used at the		Max. density value	Calculated molar ratios [Au] : [P]	% Error
	Intermediate intersection points (=↓)	End-point (=↓↓)			
-3	1.8	i 4.00 h	0.79	1:3↑ →1:2↓ →1:1↓↓	0.0
.0	2.3	i 3.00 h	0.49	2:3↑ →4:5↓ →1:1↓↓	0.0
.5	2.2	i 3.00 h	0.29	1:2↑ →3:4↓ →1:1↓↓	0.0
.2	2.03	i 3.00 h	0.40	2:5↑ →2:3↓ →1:1↓↓	0.0
.2	2.1; 2.9	i 4.00 h	x 0.75	1:2↓ →3:4↓ →1:1↓↓	0.0
.2	2.0	i 3.00 l.i.	xx 0.54	2:3↓ → 1:1↓↓	0.0
.9	2.3	i 3.00 h	x 0.51	2:3↑ →3:4↓ →1:1↓↓	0.0
.6				∼1:1↑	
.5		c 3.00 l.i.	0.51	4:5↑ → 1:1↓	
.3		4.00 h	0.58	2:3↑ → 2:1↓↓	0.0
.8	1.5; 2.2	i 4.00 h	0.51	2:3↑ →∼1:1↓ →2:1↓↓	0.0
.1	1.56	i 2.00 h	x 0.80	1:2↓↓	0.0
.6	(1.1)	i 1.50 h	0.62	(1:3)↑ → 1:2↓↓	0.0
.35	(1.05); c. 1.4	i 2.00 h	x 0.57	(1:4)↑ →1:3↓ → 1:2↓↓	0.0
.0	2.35	i 4.00 h	0.55	4:1↑ →∼3:2↓ → 1:1↓↓	0.0
.0	1.4; 2.3	i 4.00 h	0.43	4:1↑ →3:1↓ →∼3:2↓ →1:1↓↓	0.0
.6	0.8; 1.2	i 2.50 h	x 0.41	5:1↓ →4:1↓ → 2:1↓↓	0.0
.5	1.37	2.50 h	x 0.41	<4:1↓ → 2:1↓↓	0.0
.6	0.9; 1.5	i 2.00 h	0.58	4:1↓ →∼3:1↓ → 2:1↓↓	0.0
.7	1.2	i 2.00 h	0.55	∼4:1↓ → 2:1↓↓	0.0
.5	1.2; 2.0; 2.8	i 4.00 h	0.64	∼2:1↓ →1:1↓ →2:3↓ →1:2↓↓	0.0
.6	2.8	i 4.00 h	x 0.54	2:3↓ →1:2↓↓	0.0

end-point; c = contact point; x = orange Corning filter No. 3484; xx = yellow Corning filter No. 3385.

obtained partly depended on the pH value of the solution and on whether the phenan-
throline or the gold chloride was used as titrant. Thus, at pH *ca.* 1, if gold chloride
was used as titrant (Expts. 1–7), the composition of the final compound was AuP $\downarrow\downarrow$
with both chloride and thiocyanate. At pH *ca.* 7, the results were different: in chloride
solution $Au_2P \downarrow\downarrow$ was obtained (Expts. 9a and 10), while in thiocyanate solution
(Expts. 11–13) $AuP_2 \downarrow\downarrow$ was obtained. With phenanthroline as titrant, we obtained
AuP $\downarrow\downarrow$ at pH *ca.* 1 with chloride (Expts. 14 and 15), and $Au_2P \downarrow\downarrow$ with thiocyanate
(Expts. 16 and 17). At pH *ca.* 7, we obtained $Au_2P \downarrow\downarrow$ with chloride (Expts. 18 and 19),
while with thiocyanate, $AuP_2 \downarrow\downarrow$ (Expts. 20 and 21). The sensitivity of the reaction,
i.e. the maximum density value obtained for a given quantity of gold, was only
slightly dependent on the composition of the final compound (Expts. 16, 17, 20 and
21). The results were not improved by the use of a filter (Expts. 20 and 21). At the
point of the initial precipitation, the following intermediate compounds were obtained
in solution: AuP_3 (Expt. 12), when titrated with gold, and $Au_4P \uparrow$ when titrated
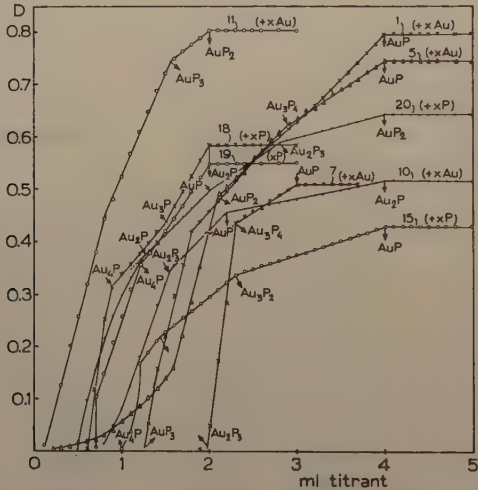with phenanthroline (Expt. 15). The titration time was 20–30 min.

Fig. 3. Titrations of gold chloride solutions with phenanthroline and the reverse.

TABLE IV

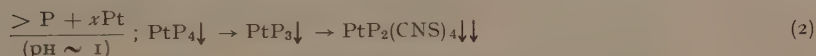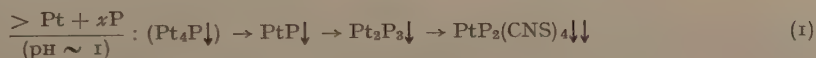| Titrant	pH	R⁻	Compound	Titrant	pH	R⁻	Compound	Titrant	pH	R⁻	Comp
	H_2PtCl_6				$PdCl_2$				$HAuCl_4$		
phenanthr.	1	Cl⁻	soluble	phenanthr.	1	Cl⁻	$Pd_2P_3\downarrow\downarrow$	phenanthr.	1	Cl⁻	Au_1P
phenanthr.	7	Cl⁻	soluble	phenanthr.	7	Cl⁻	$Pd_2P_3\downarrow\downarrow$	phenanthr.	7	Cl⁻	Au_2P
phenanthr.	1	CNS⁻	$Pt_1P_2\downarrow\downarrow$	phenanthr.	1	CNS⁻	$Pd_1P_3\downarrow\downarrow$	phenanthr.	1	CNS⁻	Au_2P
phenanthr.	7	CNS⁻	soluble	phenanthr.	7	CNS⁻	$Pd_2P_3\downarrow\downarrow$	phenanthr.	7	CNS⁻	Au_1P
H_2PtCl_6	1	Cl⁻	soluble	$PdCl_2$	1	Cl⁻	$Pd_2P_3\downarrow\downarrow$	$HAuCl_4$	1	Cl⁻	Au_1P
H_2PtCl_6	7	Cl⁻	soluble	$PdCl_2$	7	Cl⁻	$Pd_2P_3\downarrow\downarrow$	$HAuCl_4$	7	Cl⁻	Au_2P
H_2PtCl_6	1	CNS⁻	$Pt_1P_2\downarrow\downarrow$	$PdCl_2$	1	CNS⁻	$Pd_1P_3\downarrow\downarrow$	$HAuCl_4$	1	CNS⁻	Au_1P
H_2PtCl_6	7	CNS⁻	soluble	$PdCl_2$	7	CNS⁻	$Pd_2P_3\downarrow\downarrow$	$HAuCl_4$	7	CNS⁻	Au_1P

DISCUSSION

reactions of noble metal halides with phenanthroline are interesting because of variety of the final compounds which were stoichiometrically and quantitatively ained at the first maximum optical density points. A further report will show that presents special advantages for the determination of the metals in alloys or in luble mixture of chlorides of all the three metals concerned. The working condi- s can be varied very easily.

he present paper deals with the most probable structures of the different, and ecially the final, compounds obtained. In each case, the sequence of intermediates ch led to the final compound are also considered. Table IV lists the working ditions under which each of the final compounds was obtained.
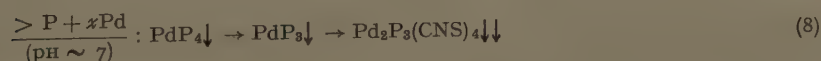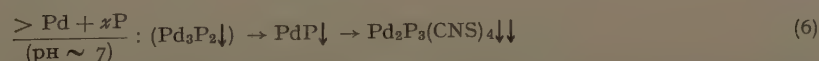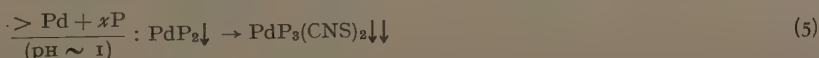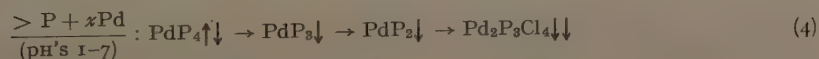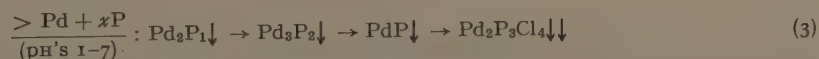
t is interesting to note that the only palladium compound, $PdC_{12}H_8N_2Cl_2$, which been used for the gravimetric determination of palladium, does not appear in experiments as a final compound, but only as an intermediate. The following sentation indicates reasonable structures for the compounds obtained.

tinum compounds

f platinum chloride was titrated with phenanthroline at *ca.* pH 1 in thiocyanate ution, or *vice versa*, (Table I, Expts. 1–6 and 11–14), the following two sequences intermediates and final compounds were derived from the curves:

$$\frac{> Pt + xP}{(pH \sim 1)} : (Pt_4P\downarrow) \rightarrow PtP\downarrow \rightarrow Pt_2P_3\downarrow \rightarrow PtP_2(CNS)_4\downarrow\downarrow \tag{1}$$

$$\frac{> P + xPt}{(pH \sim 1)} ; PtP_4\downarrow \rightarrow PtP_3\downarrow \rightarrow PtP_2(CNS)_4\downarrow\downarrow \tag{2}$$

lladium compounds

If palladium chloride was titrated at pH values 1–7 with phenanthroline, or *vice ~sa*, the same empirical final compound was always obtained, namely $Pd_2P_3Cl_4 \downarrow\downarrow$. thiocyanate was present in sufficient excess, two compounds were obtained. At pH 1 the empirical composition of the final compound was $PdP_3(CNS)_2 \downarrow\downarrow$, but *ca.* pH 7 the final compound was $Pd_2P_3(CNS)_4 \downarrow\downarrow$. The following sequences of termediates and final compounds were obtained:
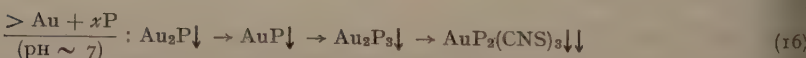
$$\frac{> Pd + xP}{(pH's\ 1-7)} : Pd_2P_1\downarrow \rightarrow Pd_3P_2\downarrow \rightarrow PdP\downarrow \rightarrow Pd_2P_3Cl_4\downarrow\downarrow \tag{3}$$

$$\frac{> P + xPd}{(pH's\ 1-7)} : PdP_4\uparrow\downarrow \rightarrow PdP_3\downarrow \rightarrow PdP_2\downarrow \rightarrow Pd_2P_3Cl_4\downarrow\downarrow \tag{4}$$

$$\frac{> Pd + xP}{(pH \sim 1)} : PdP_2\downarrow \rightarrow PdP_3(CNS)_2\downarrow\downarrow \tag{5}$$

$$\frac{> Pd + xP}{(pH \sim 7)} : (Pd_3P_2\downarrow) \rightarrow PdP\downarrow \rightarrow Pd_2P_3(CNS)_4\downarrow\downarrow \tag{6}$$

$$\frac{> P + xPd}{(pH \sim 1)} : PdP_4\downarrow \rightarrow PdP_3(CNS)_2\downarrow\downarrow \tag{7}$$

$$\frac{> P + xPd}{(pH \sim 7)} : PdP_4\downarrow \rightarrow PdP_3\downarrow \rightarrow Pd_2P_3(CNS)_4\downarrow\downarrow \tag{8}$$
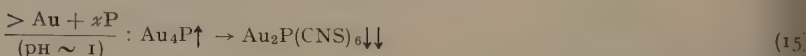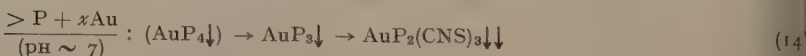
Gold compounds

Three different final compounds were obtained with gold chloride in chloride c[...] thiocyanate solutions, namely $AuP_2 \downarrow\downarrow$, $AuP \downarrow\downarrow$ and $Au_2P \downarrow\downarrow$. In the chloride solutio[...] at *ca.* pH I the final compound $AuPCl_3 \downarrow\downarrow$ was always obtained; at *ca.* pH 7 $Au_2 PCl_6 \downarrow$[...] was obtained.

In thiocyanate solution at *ca.* pH I two final compounds were obtained. If $AuCl$[...] was used as titrant, the compound was $AuP(CNS)_3 \downarrow\downarrow$, but in the reverse case Au_2P[...] $(CNS)_6 \downarrow\downarrow$ was formed. At *ca.* pH 7 both types of titrations gave the same fina[...] compound, $AuP_2(CNS)_3 \downarrow\downarrow$.

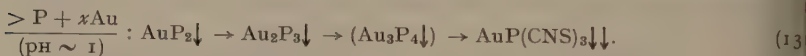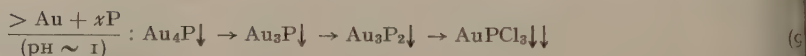The following sequences of intermediates and final compounds were obtained:

$$\frac{> Au + xP}{(pH \sim 1)} : Au_4P\downarrow \rightarrow Au_3P\downarrow \rightarrow Au_3P_2\downarrow \rightarrow AuPCl_3\downarrow\downarrow \tag{9}$$

$$\frac{> Au + xP}{(pH \sim 7)} : Au_4P\downarrow \rightarrow Au_3P\downarrow \rightarrow Au_2PCl_6\downarrow\downarrow \tag{10}$$

$$\frac{> P + xAu}{(pH \sim 1)} : (AuP_3)\uparrow \rightarrow AuP_2\uparrow\downarrow \ldots AuPCl_3\downarrow\downarrow \tag{11}$$

$$\frac{> P + xAu}{(pH \sim 7)} : Au_2P_3\uparrow \rightarrow AuP\downarrow \rightarrow Au_2PCl_6\downarrow\downarrow \tag{12}$$

$$\frac{> P + xAu}{(pH \sim 1)} : AuP_2\downarrow \rightarrow Au_2P_3\downarrow \rightarrow (Au_3P_4\downarrow) \rightarrow AuP(CNS)_3\downarrow\downarrow. \tag{13}$$

$$\frac{> P + xAu}{(pH \sim 7)} : (AuP_4\downarrow) \rightarrow AuP_3\downarrow \rightarrow AuP_2(CNS)_3\downarrow\downarrow \tag{14}$$

$$\frac{> Au + xP}{(pH \sim 1)} : Au_4P\uparrow \rightarrow Au_2P(CNS)_6\downarrow\downarrow \tag{15}$$

$$\frac{> Au + xP}{(pH \sim 7)} : Au_2P\downarrow \rightarrow AuP\downarrow \rightarrow Au_2P_3\downarrow \rightarrow AuP_2(CNS)_3\downarrow\downarrow \tag{16}$$

One of us (M.B.) is preparing a special report dealing with the structures of nitrogen[...] compounds with the noble metal halides. Therefore only a few structures, mostly of[...] final compounds are presented here.
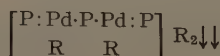
Thus, the $PtP_2(CNS)_4 \downarrow\downarrow$ in equations (1) and (2) probably has the structure

$$\begin{bmatrix} P:Pt:P \\ (CNS)_2 \end{bmatrix} (CNS)_2\downarrow\downarrow,$$
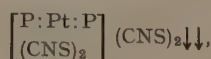
while the primary intermediate compound in equation (2) may have the structure

$$\begin{bmatrix} P \\ \cdot \\ P:Pt:P \\ \cdot \\ P \end{bmatrix} (CNS)_4\downarrow$$
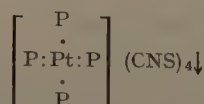
The final palladium compound $Pd_2P_3R_4 \downarrow\downarrow$ in equations (3), (4), (6) and (8) may[...] be represented as:

$$\begin{bmatrix} P:Pd \cdot P \cdot Pd:P \\ R \qquad R \end{bmatrix} R_2\downarrow\downarrow$$

ile the compound $PdP_3(CNS)_2$ ↓↓ in equation (5) may have the structure:

$$\left[\begin{array}{c} P \\ : Pd : P \\ P \end{array}\right] (CNS)_2 \downarrow\downarrow$$
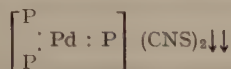
e following may be stated regarding the gold compounds obtained: $AuPR_3$ ↓↓, tained in equations (9), (11) and (13), may be shown as: $[R_2Au : P]R$ ↓↓. Au_2PR_6 ↓↓ in equations (10), (12) and (15) may be shown as the salt complexes: $: AuR_2] [AuR_4]$ ↓↓, $[P : Au : P] [AuR_4]_3$ ↓↓ or as a complex compound: $R_3Au.P.-$ R_3 ↓↓. The formation of one or the other depends on the pH value, on the titrant ed, and on the halide participating in the complex formation. The compound $P_2(CNS)_3$ ↓↓ was obtained at pH 7 only (eqn. 14 and 16) and may be represented $[P : Au : P] (CNS)_3$ ↓↓.

SUMMARY

e reactions between platinum, palladium and gold halides and phenanthroline were studied terometrically. By changing the composition of the solutions, six different final compounds re obtained. Each of the compounds could be used for the determinations of the metals. The ors were one per cent or less. The most probable structural formulae for the final compounds e presented.

RÉSUMÉ

s auteurs ont effectué une étude hétérométrique des réactions et des composés obtenus entre halogénures de platine, de palladium et d'or, et la phénanthroline. Chacune de ces réactions ut servir au dosage de ces trois métaux.

ZUSAMMENFASSUNG

e Reaktionen zwischen Platin-, Palladium- und Goldchlorid und Phenanthrolin sowie die sammensetzung der Reaktionsprodukte wurden heterometrisch untersucht. Diese Reaktionen nnen zur Bestimmung der drei Metalle verwendet werden.

REFERENCES

D. E. RYAN, *Analyst*, 77 (1952) 46; *Can. J. Research*, 27B (1949) 67, 938; F. E. BEAMISH, *Talanta*, 1 (1958) 3; *Anal. Chim. Acta*, 20 (1959) 101; C.DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam 1953; W. W. BRANDT, F. P. DWYER AND E. D. GYARFAS, *Chem. Revs.*, 54 (1954) 959.
See literature on heterometry, *Anal. Chim. Acta*, 20 (1959) 15, 227 and 357; M. BOBTELSKY, *Heterometry*, Elsevier, Amsterdam 1960.

Short Communications

The behaviour of pyro- and tripoly-phosphate complexes at the dropping mercury electrode

hether or not covalent bonding as well as electrostatic attraction plays a part in e stabilization of the metal complexes of straight chain polyphosphates[1], the close ructural similarity between pyrophosphate and tripolyphosphate ions should sult in their metal complexes having similar properties. A study of their behaviour the dropping mercury electrode is therefore of interest. Some of the preliminary ta obtained in this connection are reported below.

The half-wave potentials for the cathodic waves of a few metals obtained in aqueous

pyrophosphate and tripolyphosphate media are given in Table I (literature values for the half-wave potentials of the simple metal ions in solution are included for comparison). All the metals give single steps which are well-developed and free from maxima. For a given metal, the resemblance between the two waves in the two phosphate media is striking. The diffusion plateau for the niobium step in either phosphate is somewhat masked by the discharge of the supporting electrolyte. Separation of the niobium step from the final current rise is, however, obtained in the derivative polarogram ($E_{d.e}$ vs. $di/dE_{d.e}$). At pH 5 the wave for lead is reversible in both the phosphates. Waves for the other metals listed in Table I (including those for lead at pH 7) are all irreversible. Reversible waves in pyrophosphate media have been reported[2,3] for a few metals but the waves become irreversible at higher pH. Very few data are available for waves in tripolyphosphate media[4].

Half-wave potentials of irreversible steps cannot of course be directly correlated to the dissociation constants of the complexes, but they qualitatively reflect the relative stabilities. It may be observed from Table I that the differences in the half-

TABLE I

REDUCTION OF PYRO- AND TRIPOLY-PHOSPHATE COMPLEXES AT THE DROPPING MERCURY ELECTRODE

Electrolyte composition: 0.5 mM depolarizer under test, 0.1 M sodium pyro- or tripoly-phosphate, ionic strength adjusted to 1.2 with sodium perchlorate. T = 30° ± 1°

Depolarizer	pH	Buffer	$E_{\frac{1}{2}}$ vs. S.C.E. in V in pyrophosphate	$E_{\frac{1}{2}}$ vs. S.C.E. in V in tripolyphosphate	$E_{\frac{1}{2}}$ vs. S.C.E. in V for simple metal ions
Pb^{+2}	5	Phthalate	—0.485	—0.524	—0.38 (1 M $HClO_4$)
	7	Phosphate	—0.580	—0.605	
Bi^{+3}	5	Acetate	—0.277	—0.344	+0.02 (0.7 M $HClO_4$)
	7	Phosphate	—0.589	—0.685	
Ti^{+4}	2		—0.372	—0.316	—0.81 (0.1 N HCl)
Nb^{+5}	7	Unbuffered	ca. —1.6	ca. —1.6	—0.455 (conc. HCl)

In the case of Nb^{+5}, the tripolyphosphate concentration was 0.2 M and consequently the ionic strength was higher

wave potentials between the simple metal ions, lead, bismuth, titanium, and their respective complexes are slightly more for the tripolyphosphate complex than for the pyrophosphate complex. This is in accord with the generally observed fact that the stability of a complex formed with a chain phosphate increases with the number of phosphorus atoms in the chain.

Surface-active materials which are strongly adsorbed on the mercury drop tend to retard or suppress these waves[4]. For example, when 0.01% gelatin is added to the base electrolyte, the waves for bismuth, titanium and niobium in both the phosphates are seriously distorted. The effect on the lead wave is less pronounced. Addition of 0.01% camphor displaces these waves to more negative potentials. As a result, the half-wave potentials of lead, bismuth and titanium in both the chain phosphates shift to around —1.0 V. The niobium wave in either phosphate remains unaffected probably because its half-wave potential (ca. —1.6 V) is beyond the desorption potential of camphor[5] (ca. —1.3 V). Conversely, gelatin, which is not completely

orbed[6] even at the discharge potential of potassium, obliterates the complexed
ium waves. Similar effects of camphor and gelatin on other polarograms have
n observed[5,7] by others. It is believed that in such cases adsorption of the depo-
zer on the mercury surface is a prerequisite for electro-reduction to occur.

fuller account of the work will be published shortly.

he authors wish to thank Dr. J. GUPTA for helpful advice and encouragement.

ional Chemical Laboratory,   P. R. SUBBARAMAN
na (India)   P. S. SHETTY

R. VAN WAZER AND F. C. CLAYTON, Chem. Revs., 58 (1958) 1011.
A. LAITINEN AND E. I. ONSTOTT, J. Am. Chem. Soc., 72 (1950) 4729.
S. SUBRAHMANYA, J. Indian Inst. Sci., 38A (1956) 87, 163.
R. SUBBARAMAN, N. R. JOSHI AND J. GUPTA, Anal. Chim. Acta, 20 (1959) 89.
M. KOLTHOFF AND C. BARNUM, J. Am. Chem. Soc., 63 (1941) 520.
F. ORLEMANN AND I. M. KOLTHOFF, J. Am. Chem. Soc., 64 (1942) 833.
A. LAITINEN AND E. I. ONSTOTT, J. Am. Chem. Soc., 72 (1950) 4565.

Thermal properties of iron(II) ethylenediammonium sulfate

on(II) ethylenediammonium sulfate 4-hydrate, $FeSO_4 \cdot (CH_2NH_3)_2SO_4 \cdot 4H_2O$,
s been suggested as a primary standard for oxidative titrimetry[1-3] and is commer-
ally available in a highly purified form intended for this purpose. However, a search
the literature does not show that a study has been reported on the thermal stability
this compound.

For the present work, a sample of iron(II) ethylenediammonium sulfate 4-hydrate,
imary standard grade, was obtained from the G. Frederick Smith Chemical Co. and
bjected to thermogravimetric examination and differential thermal analysis
TA). The thermobalance and the DTA apparatus have been previously described[4,5].

The thermobalance and DTA thermal decomposition curves of the compound are
ven in Fig. 1. Using as an example a sample weighing 78.0 mg, curve A in Fig. 1 was
tained. The compound was stable up to 125°, at which point it began to lose water
hydration, the process being completed at 238°. This first weight loss corresponded
the evolution of 4 moles of water per mole of compound as evidenced by the data:
ater lost, 17.8%; theoretical weight loss for $4H_2O$, 18.0%. It is to be noted that a
houlder occurs at 175°, suggesting that the water is eliminated in two equal steps.
eyond 295°, a further weight loss occurs, terminating at 475°, which corresponds
ughly to the loss of $(CH_2NH_3)_2SO_4$. Beyond this temperature, the iron(II) sulfate
egan to decompose to the oxide, iron(III) oxide; however, the process was not com-
leted. The loss of weight between 295 and 475° is about 10% less than the theoretical
alue; it is supposed that this is caused by the oxidation of some of the $FeSO_4$ to the
xide.

The DTA thermal decomposition curve of the compound is shown in curve B of Fig. 1. Two well-defined endotherms are present at 140° and 210°, which corresponds to the loss of the hydrate water. The other peaks obtained do not lend themselves to easy interpretation but do represent the decomposition of the anhydrous compound
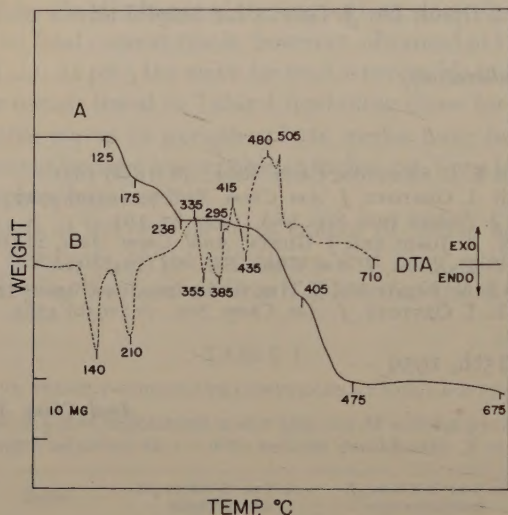

Fig. 1. Thermal decomposition of iron(II) ethylenediammonium sulfate 4-hydrate. Curve A. Thermobalance curve. Curve B. DTA curve.

to iron(III) oxide. The peak maximas are obtained at different temperatures than those found on the thermobalance curve because of the different furnace conditions and also heating rates employed.

From the above information, it may be concluded that the iron(II) ethylenediammonium sulfate 4-hydrate can be safely dried at a temperature of 105 to 110° in air without danger of decomposition or oxidation. The anhydrous salt, is stable in the 238 to 295° temperature range, at the heating rate employed.

Department of Chemistry, Texas Technological College,   WESLEY W. WENDLANDT
Lubbock, Texas (U.S.A.)   GALEN W. EWING
and
Department of Chemistry, New Mexico Highlands University,
Las Vegas, N.M. (U.S.A.)

1 K. F. CARAWAY AND R. E. OESPER, *J. Chem. Educ.*, 24 (1947) 235.
2 H. DIEHL AND G. F. SMITH, *Quantitative Analysis*, John Wiley and Sons, New York 1952.
3 A. J. NUTLER, *Anal. Chim. Acta*, 3 (1949) 433.
4 W. W. WENDLANDT, *Anal. Chem.*, 30 (1958) 56.
5 W. W. WENDLANDT, *J. Chem. Educ.*, 37 (1960) 94.

Received December 23rd, 1959

BOOK REVIEW

Analysis of Titanium and its Alloys, 3rd Ed., Imperial Chemical Industries Ltd., The Kynoch Press, Birmingham 1959, Pp. 119. Price 21 s.

Many problems peculiar to nuclear reactors, travel in the atmosphere and in outer space, corrosion, etc. have been satisfactorily solved by using unconventional materials such as titanium, zirconium, beryllium, and their alloys. Until recently, these materials have not been available commercially and there has been a corresponding lack of methods for their analysis published in the scientific literature. This situation was partly remedied by the appearance, in 1956, of the manual "*The Analysis of Titanium and its Alloys*", an outcome of the considerable research carried out by Imperial Chemical Industries (I.C.I.) Ltd. in the field of titanium technology.

Since 1956, further rapid progress in titanium technology has ensured that analytical methods be kept under constant review. Modifications and replacements of earlier procedures, together with methods for determination of additional elements, both as impurities and as alloying constituents, soon appeared in the form of a second edition (1957) of the manual.

Current procedures are contained in the recent third edition, in which the high standard one has grown to expect from all I.C.I. publications, is maintained. Although the layout of previous editions has been preserved, methods of analysis are now presented under 28 different section headings. It is interesting to note from the bibliography that much of the original work has in fact been contributed by I.C.I. itself.

Several procedures appear for the first time in the third edition: absorptiometric determination of boron with curcumin, following preliminary separation of boron by distillation as methyl borate, a simplified low-pressure method for routine determination of carbon, differential absorptiometric determination of alloying amounts of molybdenum, a method not subject to interference from tungsten as is the previously recommended gravimetric procedure using α-benzoinoxime, and absorptiometric determination of low amounts of nitrogen via the sensitive indophenol colour reaction. Turbidimetric determination of small quantities of chlorine has been replaced by a simple, yet elegant, amperometric procedure. A feature of the third edition is a statement of the reproducibility attainable with every procedure. In order to readily differentiate between titanium and its alloys, a short section has been added on spot test procedures. A table of atomic numbers and weights has also been included and, in the reviewer's opinion, logarithmic tables might usefully be incorporated into any future edition.

As to be expected from work in a field still so relatively new, several previously recommended procedures have now been modified in the light of further experience. Thus, absorptiometric determination of chromium with diphenylcarbazide has been largely re-written, copper below 0.05% is now determined by means of the chloroform-extractable diethyldithiocarbamate complex instead of with bis-cyclohexanone oxalyldihydrazone, determination of phosphorus below 0.5%, as for higher amounts, is still based on formation of the yellow phospho-vanadomolybdate complex but solvent extraction of the latter with amyl alcohol–ether is recommended, and the "gettering" effects of manganese, when determining oxygen in titanium–manganese alloys by vacuum fusion, has been overcome. The use of high-frequency (R.F.) induction heating of samples for the determination of hydrogen by vacuum extraction, statement of the interference of molybdenum, chromium, nickel and vanadium, in the method for determination of iron and how to overcome this, how to counteract the interference of iron in the absorptiometric determination of nickel, and the need for blanks on tin-free titanium in the determination of tin, are but a few of the more minor modifications to the text of the second edition.

In the section on phosphorus determination, "containing more than 3% manganese" (p. 85) should surely be "less than", while no reference is made to "Note I" in the text detailing flame photometric determination of sodium, although a Note I (p. 92) subsequently follows. These are the only errors which have been detected, the typography being excellent.

Minor criticisms of the text are the need to enlarge on "It is recommended . . . pick-up of boron" (p. 18) and "then remove the oxide layer" (p. 19), while instead of "titrate the chromate" (p. 106) it would be preferable to say "titrate the dichromate", which would be the state of the anion in sulphuric acid solution. Of more importance, however, is the failure to mention precautions for satisfactory weighing of a hygroscopic precipitate such as calcium oxide (p. 22). In any case it would seem better to convert the oxide to carbonate, a more favourable weighing form for calcium. The conversion could hardly prolong the determination since it is recommended that the calcium oxalate precipitate be allowed "to settle for 3–4 hours, preferably overnight". Because of the time already needed to produce a granular precipitate, the technique of homogeneous precipitation might be employed with advantage on this occasion.

The removal of traces of deleterious manganese dioxide, when preparing a standard solution of potassium permanganate (p. 107), could be appreciably quickened, without ill effect, by merely heating the solution at about 90° for one hour, cooling, then filtering through a calcined asbestos pad. Finally, the reviewer would like to see a note in one of the earlier sections of the manual stressing the need to remove "titanium silicate" stains from beakers, etc. with a suitable solvent as soon as possible after use. Otherwise, the stains may only be removed, if at all, with great difficulty.

In conclusion, for the uninitiated, there are many pitfalls in the specialised field of titanium analysis, inherent difficulties of sampling, use of unconventional solvents, need to avoid hydrolysis when processing titanium solutions, etc. The interested analytical public is, therefore, greatly indebted to I.C.I. for continuing to make available, at a most reasonable price, its wealth of experience in this field. Perhaps it is too much to hope that, eventually, either the manual may be enlarged to include methods for analysis of zirconium, beryllium, and their alloys, or possibly even that separate manuals may be published on these subjects.

M. WILLIAMS (Birmingham)

REVUE DE LIVRE

The Chemical Society Annual Reports on the Progress of Chemistry for 1958, Vol. LV, Londres 1959. The Chemical Society Burlington House, London, W 1., 527 p. Prix £ 2.0.0.

Nous ne donnerons, dans ce compte rendu, que les chapitres susceptibles d'intéresser directement le chimiste analyste. C'est le cas pour le premier chapitre intitulé: Chimie minérale et chimie physique, qui traitent des progrès réalisés dans le domaine des équilibres acide–base et de la précision des déterminations thermodynamiques des constantes de ces couples en solution, effectuées à partir de la F.E.M., par spectrophotométrie ou par conductivité. On y trouve aussi un paragraphe sur l'hydrolyse des cations et un autre sur les oxy-acides en solution aqueuse. Enfin, sous le titre de ,,ions association'', les auteurs décrivent les principaux travaux effectués sur les liaisons entre ions, sur les propriétés thermodynamiques, sur la conductibilité et sur le comportement dans le visible, dans l'ultra-violet et dans l'infra-rouge, qui en découlent. Un paragraphe est consacré à l'électrochimie.

Dans cet ouvrage, 40 pages seulement sont réservées à la chimie analytique, aussi ne peut-on reprocher aux auteurs de ne donner qu'un bref aperçu des recherches faites dans ce domaine au cours de l'année 1958. Les principales rubriques sont: Généralités analyse qualitative, analyse quantitative inorganique et organique avec comme paragraphes: quantitative (gravimétrique), quantitative (volumétrique). Enfin, les méthodes physico-chimiques sont passées en revue parmi lesquelles la chromatographie, la spectrophotométrie inorganique et organique, la spectrographie, la micro-analyse, les méthodes radiochimiques et l'appareillage. Quelque 60 pages sont consacrées à la chimie inorganique, dont la plus grande partie aux éléments de transition. La chimie organique et la chimie biologique occupent une très vaste place dans ce rapport annuel.

La lecture en est agréable, elle donne un aperçu utile du développement de la chimie au cours de l'année 1958, les faits y sont exposés dans un ordre logique, dans un style concis et clair. Une table des matières et une table des auteurs permettent aux lecteurs de trouver rapidement le sujet qui les intéresse.

D. MONNIER (Genève)